



The operational viability of implementing anaerobic digestion technology to
pre-treat craft brewery wastewater in Western Australia.

Bachelors of Engineering Honours – Environmental Engineering

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I declare that this honours thesis has been composed solely by myself and that it has not been submitted for any other previous application for a degree. Except where stated otherwise by reference or acknowledgment, the work presented is entirely my own.

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Abstract

Operational difficulties associated with the rapid build-up of aerobic sludge, has resulted to irreversible damage to a series of ultrafiltration membranes at a local brewery. High chemical oxygen demand (COD) ($\approx 1654.7 \pm 588.5 \text{ mg/L}$) and total suspended solids (TSS) concentrations ($\approx 235.5 \pm 100.3 \text{ mg/L}$) of the raw brewery wastewater has been identified as the cause of the excess build-up of sludge in the onsite moving bed biofilm reactor (MBBR). The downstream damage associated with the rapid generation of sludge is in excess of AUD94,600 per year. This thesis project investigates the operational viability of using anaerobic digestion (AD) technology to pre-treat the raw brewery wastewater to determine the resultant downstream effect of AD on the ultrafiltration (UF) membranes. This was achieved by conducting a pilot scale study (investigating the relationship between the hydraulic retention time (HRT) and temperature on COD removal, TSS removal and biogas generation) and a bench top study (investigating the maximum degradability of brewery wastewater via AD was also assessed in this project along with the maximum biogas generation potential of the waste stream).

Results from this study suggest that the addition of an AD system would achieve a 75.9% and 89.6% increased reduction of COD and TSS respectively compared to the current MBBR system at a digestion temperature of 20°C and a residence time of 5 days. Reducing the reactor temperature and wastewater residence time would negatively affect the AD process, with COD and TSS removals of 61.2% at 18°C and 66% at 3 days detention times noted respectively. Mathematical modelling of the AD process suggests that UF will no longer be necessary, as the quality of the effluent would meet the wastewater discharge limits set by local authorities ($\leq 30 \text{ mg/L TSS}$). The downstream effects of the proposed system suggest that an operational expenditure (OPEX) recovery between AUD37,500 and AUD50,000 per annum can be achieved by reducing the damage to the UF membranes.

This research found that, for the AD of brewery wastewater an activation energy (E_a) in the range of 20.41 kJ/mol.K to 20.09 kJ/mol.K for an upflow type reactor is required. The Arrhenius constant (θ) for the treatment process ranges between 1.03 and 1.09 at 30°C and 22°C respectively.

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Nomenclature

AD – Anaerobic Digestion	MLVSS – Mixed Liquor Volatile Suspended Solids
BOD – Biochemical Oxygen Demand	OLR – Organic Loading Rate
CAPEX – Capital Expenditure	OPEX – Operational Expenditure
COD – Chemical Oxygen Demand	PFD – Process Flow Diagram
CODs – Soluble COD	PP – Payback Period
COD _t – Total COD	SRT – Solid Retention Time
COD _p – Particulate COD	SS – Suspended Solids
EEI – Environmental Engineers International Pty. Ltd.	TAN – Total Ammonia Nitrogen
FTIR – Fourier Transform Infrared Spectroscopy	TSS – Total Suspended Solids
GC-TCD – Gas Chromatography Thermal Conductivity Detector	UF – Ultrafiltration
IBC – Intermediary Bulk Container	VFAs – Volatile Fatty Acids
MBBR – Moving Bed Biofilm Reactor	VSS – Volatile Suspended Solids
MCRT – Mean Cell Residence Time	WWTP – Wastewater Treatment Plant

Chapter 1: Introduction.

A beverage enjoyed by millions around the world, beers and ales are produced by fermenting raw ingredients such as malt, hops and barley with yeast. This process is more commonly known as the brewing process [1]. Brewing beers and ales is a complex and water intensive process which generates between 3L-10L of wastewater for every 1L of beer produced [2]. The brewing process produces a wastewater which is nutrient rich, easily biodegradable and contains high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) concentrations [2]. Wastewater generated from beer breweries generally contains high concentrations of organic substances such as soluble starches, sugars, volatile fatty acids (VFAs), suspended solids (SS) and even ethanol in the form of spent beer [3]. Wastewater of such characteristics requires treatment before safe environmental discharge can occur.

One method of brewery wastewater treatment is through the use of a moving bed biofilm reactor (MBBR) to aerobically reduce BOD and nutrient (mainly nitrogen) concentrations. This method of brewery wastewater treatment was adopted by a local craft brewery located in Baldivis, Western Australia in 2016 [4]. Operational reports from the brewery indicated that, the onsite MBBR wastewater treatment plant (WWTP) was experiencing difficulties (frequent fouling of the ultrafiltration (UF) membranes) which reduced the lifespan of the membranes (from 3 years to 6-12 months). This was amounting to increased operating costs (in excess of AUD94,600 per year – breakdown included in Appendix E). The manufacturers of the UF membranes attribute the frequent fouling to the high turbidity in the wastewater being treated by the UF membranes (caused by high SS concentrations) [5].

Considering the client's available space and the issue at hand, *Environmental Engineers International Pty. Ltd.* (EEI) proposed using anaerobic digestion (AD) technology, to reduce

the COD of the raw brewery wastewater before it is treated by the MBBR unit. The lowered COD concentrations of the wastewater is expected to reduce the quantity of sludge generated in the MBBR, consequently reducing the concentrations of total suspended solids (TSS) in the wastewater being treated by the UF membranes. However, as an AD system for the pre-treatment of brewery wastewater has never been operated or trialled in Australia for this application, the downstream effects of using AD on the MBBR and UF membranes was largely unknown.

1.1 Problem Identification.

High concentrations of COD in the brewery wastewater has been attributed to the rapid generation of sludge in the MBBR unit, which has resulted in frequent fouling and irreversible damage to the UF membranes used. Figure 1 shows the sludge removed from 6 of the UF membranes after backwashing and chemical cleaning.



Figure 1: Sludge sample removed from the UF membranes [6].

To prevent this from occurring, an AD unit is proposed to be implemented to reduce the COD concentrations of the raw wastewater entering the MBBR unit. The reduced COD concentrations is expected to lower the amount of sludge generated in the MBBR, consequently reducing the fouling frequency and damage associated with the frequent fouling of the UF membranes.

1.2 Project Aims.

With the brief presented, this industry-based thesis project is aimed at delivering information regarding:

1. The degradability of COD and TSS of the raw brewery wastewater via low temperature ($< 25^{\circ}\text{C}$) anaerobic digestion.
2. The activation energy and Arrhenius constant of low temperature brewery wastewater treatment using AD technology.
3. The predicted downstream effects of the lowered COD and TSS concentrations on the WWTP (specifically fouling of the UF membranes) via a series of mathematical models.
4. The potential viability of using the biogas generated from the AD process as a supplementary fuel source for cooking in the tavern restaurants and kitchens located onsite.

1.2 Project Hypothesis and Research Process.

It is hypothesised that the implementation of an AD at the client's craft brewery will reduce the concentration of COD and TSS in the raw wastewater, the amount of sludge generated in the MBBR unit and also increase the lifespan of the UF membranes by several years.

Figure 2 represents the research process used to answer the project aims and hypothesis.

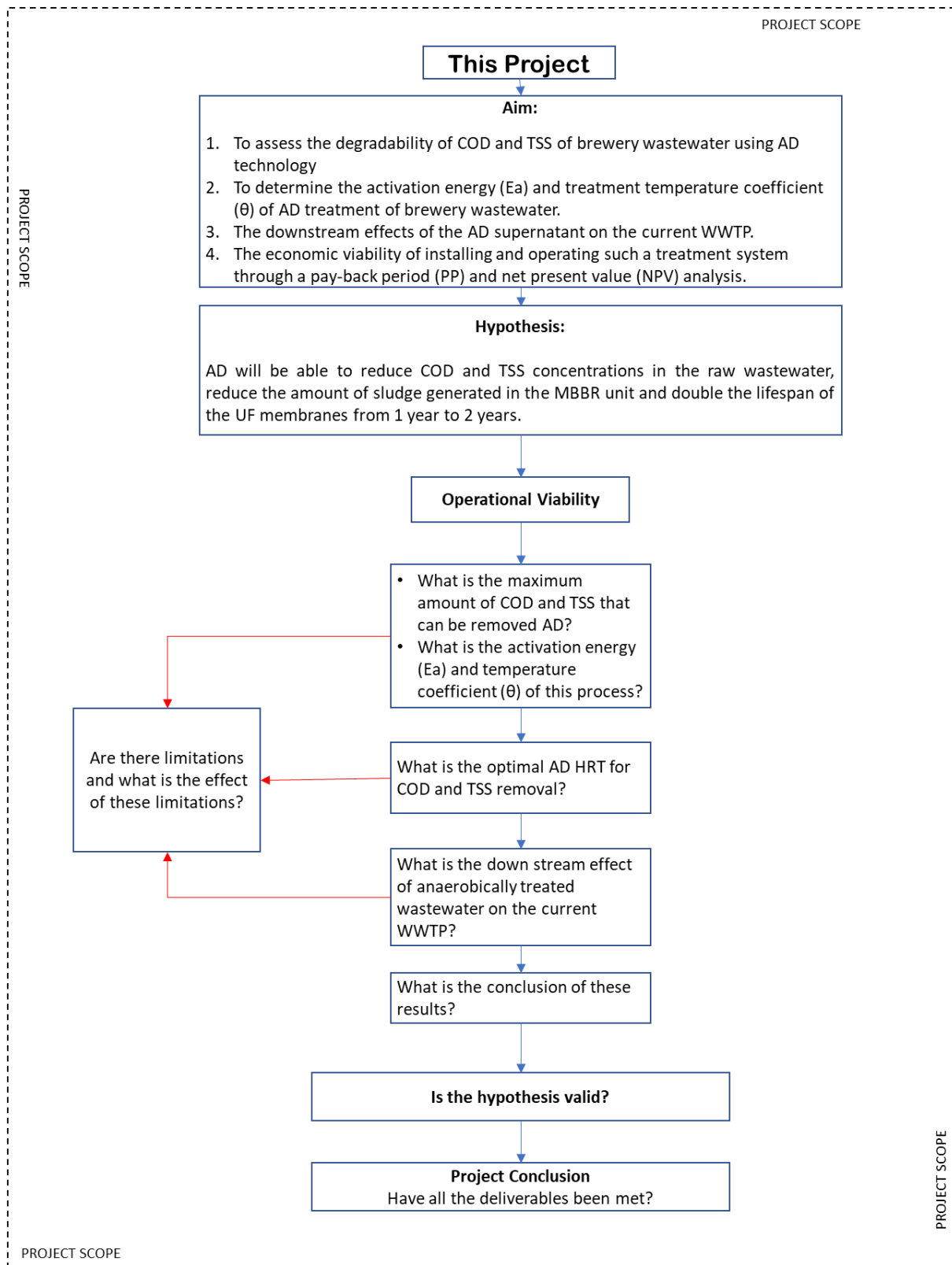


Figure 2: Research approach used to answer the project's hypothesis.

1.3 Project Scope

Due to the size and complexities associated with this engineering project, the scope of this project was narrowed to consider the following key areas.

- i. A detailed site investigation and current WWTP operations via baseline data collection of the influent and treated wastewater at the WLB brewery.
- ii. Laboratory analysis of; wastewater quality parameters such as; TSS, COD, pH and biogas quality analysis of the raw wastewater, wastewater from the MBBR and the influent and effluent wastewater from the batch and continuous studies.
- iii. The design, construction and commission of a pilot plant study assessing the suitability of treating WLB wastewater using a pulse fed up flow AD unit.
- iv. Modelling of COD and TSS destruction/generation in the AD and current WWTP, biogas formation and sludge generation from the anaerobic and aerobic processes via experimental data
- v. An assessment of the extent the biogas generated from AD can be used to improve financial viability.

The complexity of the mathematical models developed are expected to fit between approximations/rules of thumb (based on simple models) and models which consider environmental factors such as reactor pressures, hydrogen concentrations etc (complex multidimensional models);

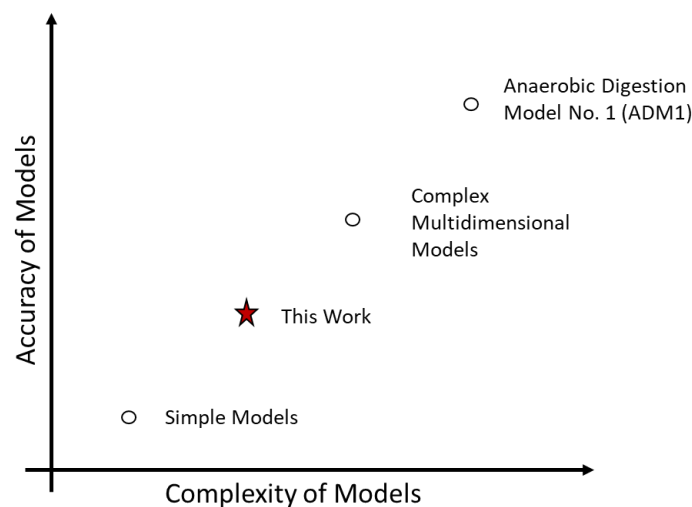


Figure 3: Complexity and scope of the models developed in this thesis versus other approaches.

1.4 Location & Site Description

The client's property is located in the City of Rockingham, Western Australia. Figure 4 represents a drone captured aerial image of the entire site, with key points of interest illustrated.

Only wastewater generated from the brewhouse is treated by the onsite WWTP. No municipal waste or faecal waste is treated via the WWTP. The WWTP consists of an MBBR unit which was constructed by Klar-Bio (Model #: Klar-Bio 40) coupled with several UF units – Figure 5. It is important to keep in mind that the wastewater generated is primarily from the brewing process, for some of the assumptions and characterisations made later in this thesis.



Figure 4: Drone captured image of the client's property [7].



Figure 5: The MBBR unit installed at the client's property, constructed by Klar-Bio [6].

1.5 Current Wastewater Treatment System

The wastewater treatment process installed at the client's craft brewery can be separated into 4 stages; 'Wastewater Generation', 'Raw Wastewater Storage', 'Wastewater Treatment' and 'Post Treatment Storage'.

At present, the client's craft brewery produces a maximum throughput of 15,000L of wastewater per day during water intensive brew days. However, daily wastewater generation during summer months is placed between 10,000 – 12,000L on average, but can be as low as 8,000L-9,000L during the winter months [8].

The current wastewater treatment train and & proposed location for the AD unit as suggested by EEI has been illustrated in Figure 6.

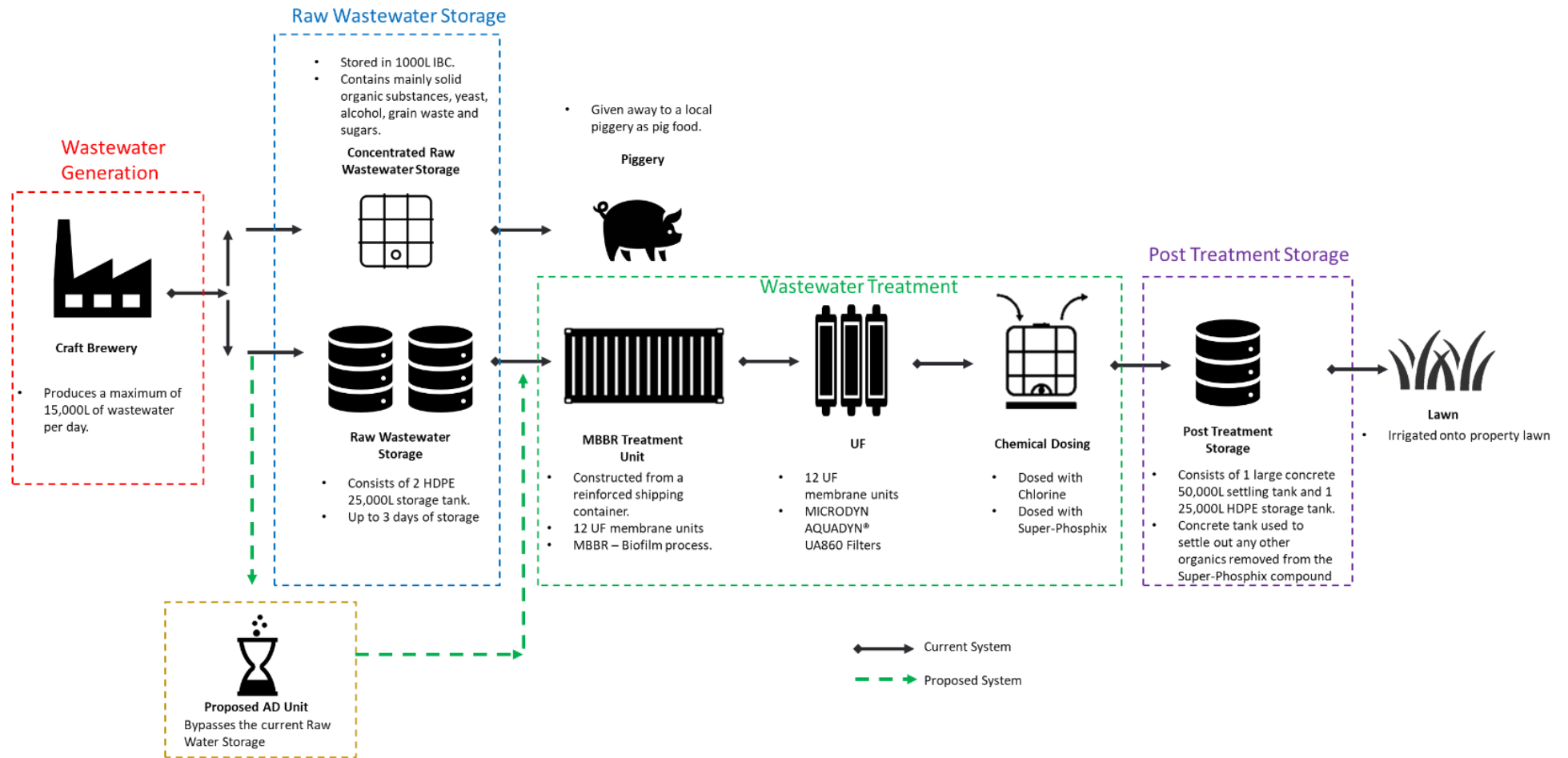


Figure 6: Simplified wastewater treatment process operated at the client's brewery along with the proposed location of the AD unit.

1.5.1 Wastewater Generation

Wastewater is generated at various points along the brewing process. Wastewater from breweries generally originate from water used during mashing, fermenting, filtration, cleaning or in the form of undesired beer [9]. The process of brewing beer along with points of wastewater generation (blue stars) have been illustrated below;

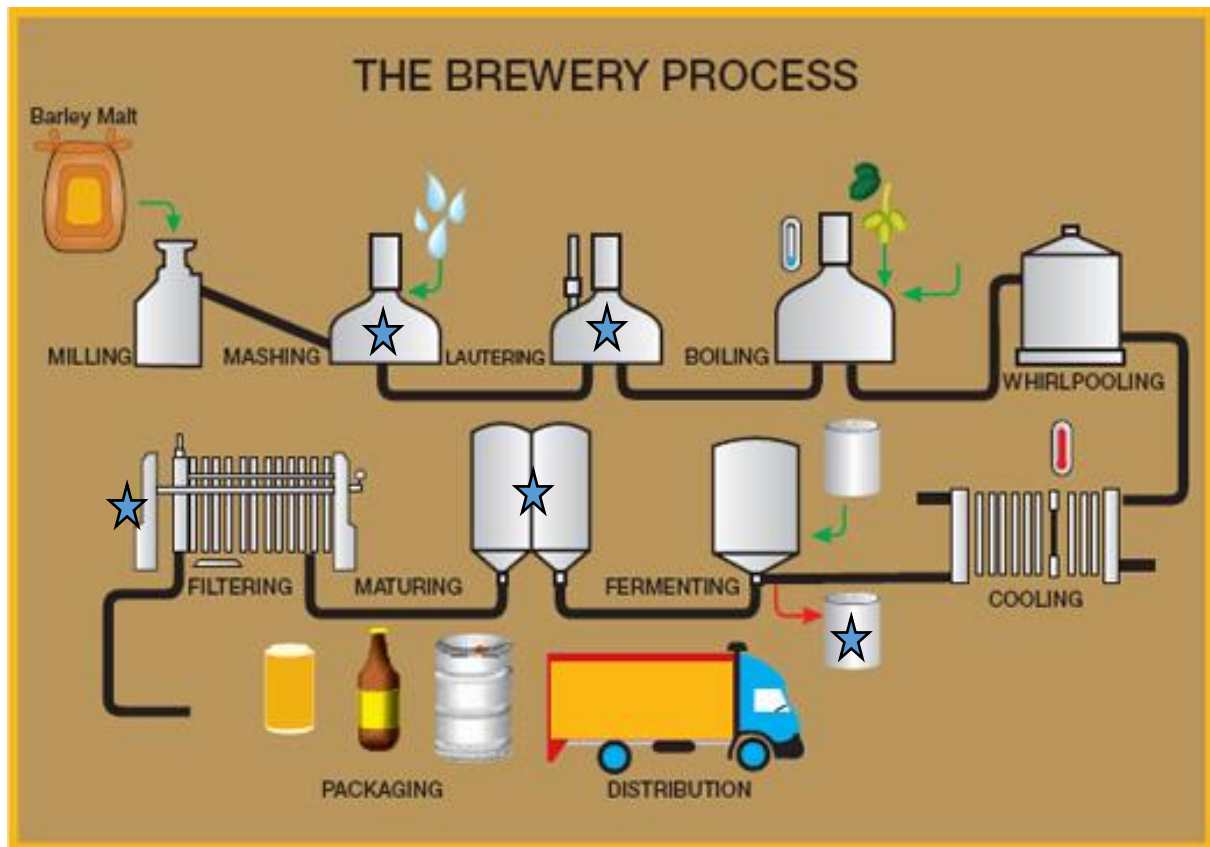


Figure 7: A simplified illustration of the brewing process [10]

1.5.2 Raw Wastewater Storage

Raw wastewater generated from the brewing process is stored in two 25,000L HDPE storage tanks – Figure 8. The storage tanks act as buffering tanks for the MBBR unit and also provide up to 3 days of emergency wastewater storage, should the WWTP require emergency shut-down. The filtered concentrated raw wastewater mainly contains spent grain husks and yeast. It is stored in several intermediate bulk containers (IBC) which are then given to local farmers as pig food - Figure 9.



Figure 8: Two 25,000L HDPE storage tanks, used to collect and store raw wastewater generated from the brewing cycle [6].



Figure 9: Intermediate bulk containers (IBC) used to store the filtered concentrated grain wastewater. These are then given away to local farmers as pig food [6].

1.5.3 Wastewater Treatment

Before the raw wastewater is pumped into the MBBR unit, it is passed through a small bag filter where any remaining particles ($>2\text{mm}$) are removed. A MBBR unit is used at the client's

brewery due to the reactor's ability to remove high concentrations of organic pollutants (often up to 98%) and nitrogen species present in the wastewater stream [11]. A schematic of the MBBR unit can be found in the Appendix A of this project.

Chamber 1 to 3 (Illustrated in Figure 35) in the MBBR unit is responsible for the aeration of the wastewater being treated and contains the bulk of the MBBR carriers. Chamber 4 is an unaerated chamber and usually does not contain any MBBR carriers. Chamber 4 is also known as the anoxic chamber and is mainly responsible for denitrification.

The treated wastewater is then pumped into a series of UF units, where residual particulates are removed. Particulates which clog (foul) the UF units are removed via a back-flushing system and/or acid/alkali wash. It is the rapid accumulation of these particles which are attributed to the operational issues faced by the brewery. The treated wastewater is then dosed with chlorine and a phosphate removal agent (*proprietary by EEI*). The dosed water is then pumped into a central tank where any residual biomass and sludge is left to settle.

1.5.4 Post Treatment Storage

Once the dosed and treated wastewater has been left to settle in the central concrete tank - Figure 43, the top layer of the water is then decanted into a third 25,000L HDPE tank. The water at this stage is known as the 'product water' and is ready for onsite irrigation. The product water undergoes monthly testing from third party laboratories to ensure that it conforms to the guidelines established by the Western Australian Government – Department of Water & Environmental Regulations (DWER) as subject to the wastewater discharge conditions set during facility licensing.

Chapter 2: Review of Existing Literature.

2.1 Wastewater Treatment Processes.

2.1.1 Aerobic and Anaerobic Processes.

The table below represents a comparative analysis between aerobic treatments systems and anaerobic treatment systems. In the case of this project, the current infrastructure operates as an aerobic system, while the proposed system operates as a joint anaerobic and aerobic system.

Table 1: A comparison between aerobic and anaerobic wastewater treatment processes. Referenced from [11], unless otherwise stated.

Parameter	Aerobic Treatment	Anaerobic Treatment
Definition	A biological treatment process where metabolic reactions are driven by the consumption of free dissolved oxygen by aerobic microorganism.	A single or multiple biological treatment processes which occur in an environment absent of oxygen, where biodegradable matter is converted into CH ₄ , CO ₂ and other end products.
Theoretical Process	<p>Aerobic treatment usually occurs in three key phases;</p> <ol style="list-style-type: none">1. Endogenous Phase. <p>As the concentration of substrate which is available is depleted, the microbes present consume their protoplasm for energy, to maintain cell function, increasing the concentration of detritus material present in the reactor.</p> <ol style="list-style-type: none">2. Nitrification <p>This is the start of the nitrogen removal phase. Ammonia released from the endogenous phase is oxidised into nitrates.</p>	<p>Anaerobic digestion usually occurs in four identifiable phases. A illustration of the digestion process can be found in Appendix E of this report.</p> <ol style="list-style-type: none">1. Hydrolysis. <p>Hydrolysis is the conversion of particulate material into soluble substances via fermentative bacteria, which can be further reduced to simple monomers used for fermentation.</p> <ol style="list-style-type: none">2. Acidogenesis

	<p>Nitrogen removal from wastewater is a primary concern to the client's brewery due to the end use of the treated wastewater (lawn irrigation), and the licencing agreement set by the Department of Water and Environmental Regulations.</p> <p>3. Denitrification</p> <p>After nitrification, denitrification usually occurs in an anoxic environment, where nitrate nitrogen is utilised as the electron acceptor of the process.</p> <p>The entire aerobic process can be simplified into the equation presented below.</p> $2C_5H_7NO_2 + 11.5O_2 \rightarrow 10CO_2 + N_2 + 7H_2O$	<p>The second step in anaerobic digestion is acidogenesis, also known as fermentation. In this step, acidogens convert carbohydrates, proteins and lipids into monosaccharides, amino acids and low carbon fatty acids. This step results in the production of volatile fatty acids (VFA), CO₂ and hydrogen.</p> <p>3. Acetogenesis</p> <p>Acetogenesis is the process where obligate hydrogen producing acetogens further ferment the intermediate products of acidogenesis (butyrate and propionate) to produce acetate, CO₂ and hydrogen.</p> <p>4. Methanogenesis</p> <p>The final step in the anaerobic digestion process is the formation of methane. Methanogens are classified into acetoclastic and hydrogenotrophic methanogens. Acetoclastic methanogens split acetate to into methane and CO₂. Hydrogenotrophic bacteria utilize the hydrogen generated from the earlier steps as an electron donor and CO₂ as an acceptor to form methane.</p>
Biomass Growth	Aerobic bacteria have a doubling time of a few hours to a couple of days [11].	Anaerobic bacteria have a doubling time of a few days to several weeks. It is not as rapid as aerobic biomass [12].
Sludge Production	Approximately 30%-60% of the organic load can be converted into sludge in aerobic processes. This estimate serves as a good comparison for the experimental sludge generation and the sludge generation from literature.	Literature investigation on sludge generation reveals that between 5%-10% of the organic load can be converted into biomass [13], with the remainder being transformed into methane and carbon dioxide. This

		estimate serves as a good comparison for the experimental sludge generation and the sludge generation from literature.
Effect of Temperature	As aerobic treatment systems are generally open outdoor systems, they are dependent on the ambient weather, leading to extreme fluctuations. However, as with the majority of biological processes, low temperatures hinder the performance of the system. Many aerobic systems in Mediterranean climates operate between 15°C and 20°C.	<p>Operating temperatures in anaerobic systems are often considered as one of the most important design and operating conditions. In practice, anaerobic digestion is maintained between 30°C to 38°C due to the high treatment capability and high rate of biogas generation (between 0.75m³/kgVSS to 1.12m³/kgVSS destroyed).</p> <p>Low temperature anaerobic digestion (<20°C) is not often found in practice due to the high HRTs required and as such there is limited information on the subject area. A study conducted by Alvarez and Soto identified that the low operating temperature causes a reduced hydrolysis rate (limiting process) and accumulation of suspended solids.</p>
Advantages (external to project scope)	<ol style="list-style-type: none"> 1. Aerobic treatment usually achieves lower concentrations of BOD in the side streams. 2. Most suitable for treatment of nutrient rich wastewaters. 3. Low capital costs for small facilities due to the ease of construction. 4. Treatments start up is extremely rapid (a few days). 5. No risks of explosions. 6. Basic fertilizer values can be recovered in the biosolids. 	<ol style="list-style-type: none"> 1. Lower energy requirements. 2. Lower production of sludge. 3. Process produced methane, an energy source. 4. Rapid response to substrate after long periods of non-feeding. 5. Lower nutrient requirements. 6. Requires a smaller volume. 7. Can operate with higher organic loading rates (OLR), from 3.2 to 32kgCOD/m³.day for anaerobic systems versus a 0.5-3.2 kgCOD/m³.day for aerobic systems.


Disadvantages <i>(external to project scope)</i>	<ol style="list-style-type: none"> 1. High energy requirement with operating the aerators. 2. Does not produce any usable product for energy generation. 3. Treatment is significantly affected by reactor temperature. 4. Biosolids produced from aerobic digestion usually has poorer dewatering characteristics than anaerobically digested biosolids. 	<ol style="list-style-type: none"> 1. Longer start up time is usually required to cultivate sufficient biomass. 2. Potential to produce hydrogen sulfide which causes odours and is corrosive. 3. Supernatant may require further treatment (usually from an aerobic process) to meet local discharge guidelines. 4. More susceptible to reactor upsets and souring.
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2.1.2 MBBR Treatment Process

The table below reviews the treatment processes which occur in MBBR reactors, along with key differences between conventional aerobic systems as detailed in Table 1.

Table 2: Moving bed biofilm treatment processes.

Parameter	Aerobic Treatment
Definition	An extension to aerobic treatment units, MBBR treatment units use the attached growth biofilm process to treat wastewater using specialised carriers (media) which freely move in the wastewater in a controlled aeration chamber [14], [15] . Figure 10 is a picture of the MBBR carriers used at the client's brewery, and the media used in the MBBR unit.

	 <p>Figure 10: (Left) Sample MBBR carriers used at the client's WWTP. (Right) The MBBR media in the WWTP [6]</p>
Process	<p>The removal of organic pollutants and nitrogen in MBBR units is a complex process which is usually governed by substrate uptake in the biofilm layer. It usually follows a pre-treatment step (not observed in all MBBR processes), aeration of wastewater in several chambers for substrate removal and nitrification, followed by clarification in an anoxic chamber for denitrification.</p>
Advantages and Disadvantages <i>(external to project scope)</i>	<p>The main advantages of MBBR treatment processes amongst many others, is; the small reactor size needed and the simplicity of the system (as no sludge return system or management is required).</p> <p>The big disadvantage of these systems, is the high energy demand due to the aeration process, the need to use proprietary media, the limitation of phosphorus removal and the difficulty associated with maintaining the system due to the media present.</p>

2.2 Characteristics of Brewery Wastewater.

Brewery wastewater is a concoction of by-products from the brewing process with large constituents being water and ethanol from waste beer which does not meet quality standards [3], [9]. Some organic acids, grain husks and starches are also commonly found in the wastewater [3]. Several studies conducted with brewery wastewater have noted the inconsistencies in the characteristics of the wastewater stream [3], [16]. Table 3 represents a compilation of brewery wastewater characteristics determined by several other studies.

Table 3: Variances in brewery wastewater characteristics between different studies.

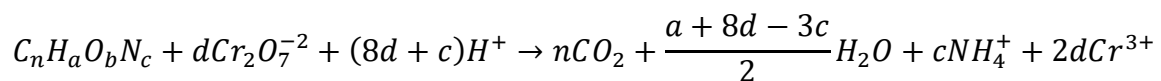
S. No	Parameter	Units	Study 1 [3]	Study 2 [16]
1.	Total Chemical Oxygen Demand (COD _t)	mg/L	5340.8±2265	2692
2.	Soluble Chemical Oxygen Demand (COD _s)	mg/L	3902.28±1644	2859
3.	Total Suspended Solids (TSS)	g/L	1.8±0.97	0.778
4.	pH	mg/L	6±1.44	7.3
5.	Total Nitrogen (TN)	mg/L	5.36	5
6.	Total Phosphorus (TP)	mg/L	-	1
7.	Conductivity	μS/cm	1520±481	-

Concerns when treating brewery wastewater with AD are:

1. The ability of any unfiltered solids from being hydrolysed.
2. Possible reactor overloading with easily biodegradable pollutants [17].
3. Lack of sufficient alkalinity.
4. The pH of the wastewater indicates it may be slightly acidic which could cause concerns of souring in the anaerobic digester.
5. Ammonia/ammonium toxicity.

2.3 Relationship Between BOD and COD.

The BOD of wastewater is often defined as the measurement of the amount of dissolved oxygen (DO) taken up by bacteria during the biochemical oxidation of organic matter [11], [18], [19]. COD on the other hand represents the measurement of the oxygen equivalent of the organic matter in the wastewater of interest which can be chemically oxidised using a dichromate in acid solution [11], [18], [20]. This is described in Equation 1.



Where: $d = \frac{2n}{3} + \frac{a}{6} - \frac{b}{3} - \frac{c}{2}$

Equation 1: Chemical oxidation of organic material using dichromate in an acidic solution [18].

COD can be broadly fractionated into the total COD (COD_t), soluble COD (COD_s) and particulate COD (COD_p) [18]. While there is debate regarding the standardised definition of COD_s and COD_p, the general consensus defines the two parameters as a function of the filter pore size used to separate the soluble and particulate components [18].

Some of the differences between the two tests are presented Table 4.

Table 4: Advantages of COD analysis instead of BOD analysis.

BOD	COD
1. The long testing time (usually 5 days is needed) [11].	1. Short testing time (between 2-3 hours is needed) [21].
2. Once the soluble organic matter has been consumed, the test loses stoichiometric validity [11].	2. COD can be fractionated into the soluble and particulate components [11].
3. A high concentration of acclimatized bacteria is needed [11].	
4. Only biodegradable organics are measured [11].	

It is for the aforementioned reasons that COD was chosen as the primary method of assessing wastewater quality. In addition to this, BOD testing facilities was not available at the time of this project. Table 5 represents the COD: BOD relationship.

Table 5: The relationship between wastewater COD and BOD [22].

COD: BOD		Biodegradability
1.	< 2	Readily Biodegradable Effluent
2.	Between 2 and 4	Moderately Biodegradable Effluent
3.	> 4	Hardly Biodegradable Effluent

2.4 Food to Microbial Ratio (F:M).

The food to microbial (F:M) ratio is defined as the relationship between the amount of food entering a reactor and the microbial biomass present in the reactor [18]. The F:M ratio is a useful parameter in estimating the concentration of organisms in substrate [23], [24]. The relationship between the food and the microbes is illustrated in Figure 11.

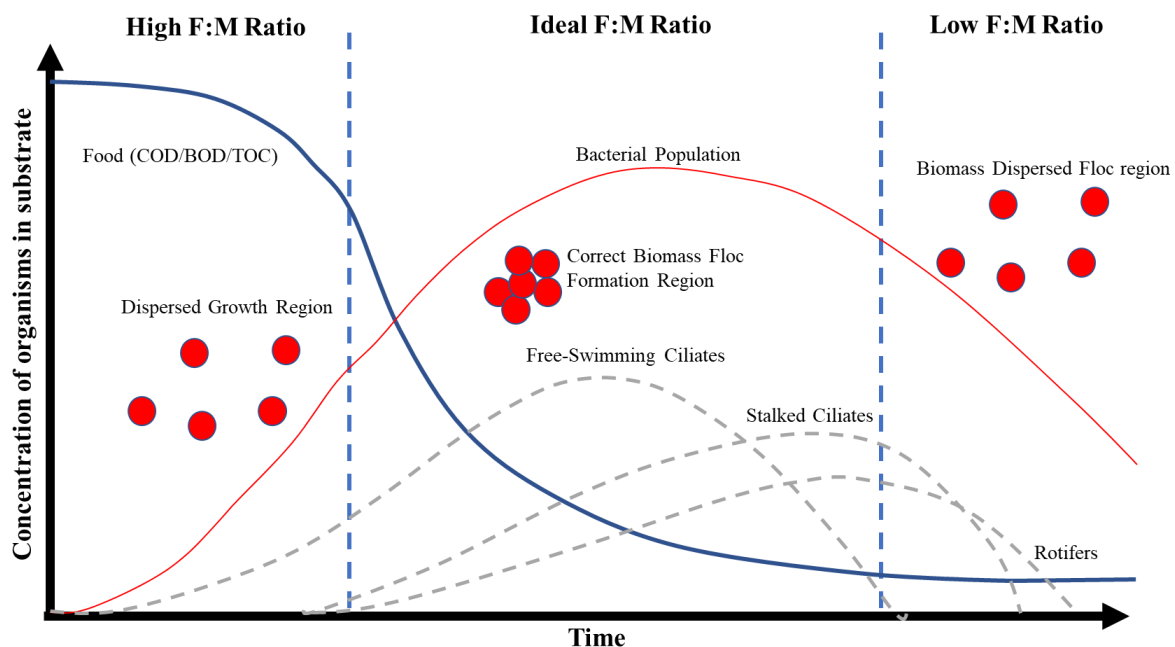


Figure 11: Relationship between the concentration of organisms in substrate versus time [23].

The F:M ratio can be expressed by the formula below:

$$F:M = \frac{\left(\text{Wastewater COD} \frac{mg}{L} \right) * \left(\text{Influent flow rate} \frac{L}{day} \right)}{\left(\text{Reactor Volume } L \right) * \left(\text{MLVSS} \frac{mg}{L} \right)}$$

Equation 2: F:M ratio formula [23], [25].

2.5 Relationship Between COD and VSS.

Volatile suspended solids (VSS) is a wastewater parameter which is most commonly used to track biomass growth in full scale reactors [18]. It is usually expressed as a concentration function in mass per unit volume (mg/L). In the case of reactors treating wastewater, MLVSS is defined as the volatile solids resulting from combining recycled sludge with influent wastewater [18]. While VSS is often used to express the growth of biomass in reactors, VSS actually consists of a concoction of active biomass, detritus cellular material and non-biodegradable VSS [18].

The concentration of VSS in a reactor can be estimated through the use of a COD/VSS conversion factor (f_{cv}). This determines the concentration of VSS based on the COD_p concentration in the reactor [26]. The conversion of COD_p to VSS has been demonstrated in Equation 3.

$$VSS \left(\frac{mg}{L} \right) = COD_p \left(\frac{mg}{L} \right) * f_{cv}$$

Equation 3: Conversion of particulate COD to VSS using a COD/VSS conversion factor [26].

A conversion factor (f_{cv}) value of 1.42mgCOD/mgVSS and is used most often for anaerobic systems [11], [18]. Conversion factors for activated sludge cultures often range between 1.39 mgCOD/mgVSS to 1.49mgCOD/mgVSS [26].

2.6 Reaction Activation Energy (E_a) and Arrhenius constants (θ).

The activation energy of a reaction can be defined as the amount of energy required to convert all the molecules in a mole of substance into a transition state [27]. It can be expressed by the Arrhenius equation - Equation 4 [11].

$$k = Ae^{-\frac{E_a}{RT}}$$

Equation 4: Arrhenius equation.

Where;

A is the pre-exponential factor.

E_a is the activation energy (J/mol).

R is the universal gas constant (8.314 J/mol.K).

T is the temperature of the system (K).

k is the reaction rate constant (time⁻¹).

The Arrhenius equation was derived by integrating the relationships between the reaction activation energy and the Boltzmann distribution [28]. The activation energy (E_a) of a chemical reaction can be used to evaluate the bioenergetics of the process at specific temperatures. In essence, evaluating if the anaerobic digestion of a substrate (in this case beer wastewater) will be favourable at different digester operating temperatures. If the free energy available is lower than the activation energy, a reaction will not occur [29].

While extensive research has been conducted which determines the activation energy of solid wastes such as cow dung, domestic waste, poultry waste, etc. Little to no information is known, regarding the activation energy of the anaerobic digestion of brewery wastewater at various temperatures. While the organic nature of brewery wastewater is commonly regarded as an easily digestible waste stream [30], an exact activation energy could not be established from literature. Table 6 is a compilation of the activation energy of common waste streams for anaerobic digestion.

Table 6: Activation energies of common waste streams for anaerobic digestion.

S.No	Waste Type	Study	Reaction Temperature (°C)	State of Waste	Activation Energy (kJ/mol)
1.	Cow Dung	[28]	40	Solid	37.82
2.	Poultry Droppings	[28]	40	Solid	37.23
3.	Combined Waste	[28]	40	Solid	26.60
4.	Domestic Waste	[28]	40	Solid	30.08
5.	Cellulose	[30]	38-65	Liquid	31±4
6.	Brewery Wastewater	This Study	17-30	Liquid	?

The Arrhenius constant of a biological process describes the dependency of reactions on temperature as shown in Equation 5: Expression used to determine the Arrhenius constant using the k values over different temperature ranges [32]. This is useful when predicting the effects, increasing or decreasing the operational temperature has on the AD process.

$$\frac{k_2}{k_1} = \theta^{T_2 - T_1}$$

Equation 5: Expression used to determine the Arrhenius constant using the k values over different temperature ranges

2.7 Characteristics of Anaerobic Sludge.

“Sludge” is often a collective term used to describe the slushy mass deposited from water and wastewater treatment processes [33]. However, the constitutions and exact characterisation of sludge is significantly more complex. While active biomass in the sludge can consume pollutants and grow, too much growth can cause significant operational expenses, mainly associated with the management of generated sludge [33].

The characteristics of sludge varies from treatment process to treatment process. However, it usually depends on the origin of the sludge and the age of the sludge [18]. Sludge can be fractionated into active biomass, detritus cellular material from endogenous respiration,

biodegradable organic substances and inert inorganic particles [34]. Sludge often has as a brown flocculant like appearance [18].

Depending on the type of anaerobic reactor, sludge can have a flocculant like appearance or a granular like appearance. Granularization of sludge occurs in 4 processes; 1. The colonisation of biomass on an inert un-colonized material or cell. 2. Adsorption of other bacterial particles by physiochemical processes. 3. Attachment of microbial biomass. 4. Multiplication of cells from substrate diffusion into granular particles [18]. Granulation is most often observed in up flow anaerobic sludge blanket (UASB) reactors [35]. Granular anaerobic sludge has several advantages over flocculant type sludge, some of which are listed below:

1. Granular sludge is stronger as it has the ability to stay together during mild mixing without falling apart [35].
2. Granular sludge can be easily stored for years with minimal deterioration [35].
3. Higher wastewater treatment efficiencies have been observed with granular sludge compared to freely suspended sludge [35].

While it is unlikely that granular sludge will be formed in the pilot reactor used to treat brewery wastewater due to the operating characteristics, generation in a full-scale plant can lead to an otherwise waste by-product becoming a second add by value product next to the biogas generated.

2.8 Modelling COD Utilization.

While COD utilization can be modelled using the same kinetics approach taken to model biogas formation. Several modifications must be made to account for the difference in the operating characteristics of plug flow reactors (PFR) compared to batch reactors. Firstly, unlike batch systems, there is an influent and effluent component to the reactor system which needs to be addressed. Secondly, and arguably the most important difference between modelling substrate

(COD) utilization in PRF is that substrate utilization is not only a function of time, but also a function of reactor length.

2.9 Modelling TSS.

Management of total suspended solids (TSS) is the key focus of this project. Defined as the portion of total solids (TS) retained on a filter of a specific size after being dried at 105°C, TSS tests are somewhat of an arbitrary measurement [18]. As TSS concentrations will vary based on the pore size of the filters used, it is important to note that TSS can be a misleading measurement. Nevertheless, it is still used as a parameter for evaluating treatment performance. TSS can be defined as per Equation 6.

$$TS = TSS + TDS$$

Equation 6: The interrelationship between TS, TDS and TSS [36].

For the purposes of this project, TSS can be modelled based on first order kinetics, similar to methods used to model substrate consumption or biogas generation. This is because the formation of TSS is usually a function of both biomass and substrate utilization. That said, an empirical relationship between the TSS and COD will be used to model TSS in the MBBR unit as the rate of solids generation is unknown.

2.10 Modelling Biogas Formation.

Biogas formation in batch reactions can be modelled using a material balance and reaction kinetics approach, or the modified Gompertz equation. It is important to note that the kinetics model can be used to model both the batch anaerobic reactors and the PRF. On the other hand, the modified Gompertz model is limited as it is only able to model the cumulative biogas production in batch reactions.

The kinetic model is based on the materials balance of the system - Equation 7.

Accumulation rate within system boundaries

$$\begin{aligned} &= \text{flow rate of reactant into the system boundary} \\ &- \text{flow rate of reactant out of the system boundary} \\ &+ \text{rate of reactant generation.} \end{aligned}$$

Equation 7: General mass balance equation for a reactant in the system [11].

The inflow rate, outflow rate and rate of reaction generation is based on the type of reactor, the defined operating parameters and the reaction order.

The modified Gompertz model is a sigmoid function which has been used successfully by several studies to model and predict the cumulative formation of biogas in a batch environment. The modified Gompertz model is based on the biogas production potential of the wastewater stream, the maximum biogas production rate, the duration of the reaction, with a lag time factor for the acclimatization of biomass. The modified Gompertz equation has been included below - Equation 8.

$$B_t = B \exp \left\{ -\exp \left[\frac{R_b \times e}{B} (\lambda - t) + 1 \right] \right\}$$

Equation 8: The Modified Gompertz first order reaction equation [37], [38].

Where;

B_t is defined as the cumulative volume of biogas generated (ml)

B is the biogas production potential of the waste stream (ml)

R_b is the maximum biogas production rate (ml/day)

λ is the lag phase associated with the addition of a new feed/environment (days)

t is the cumulative time for biogas production (days)

2.11 Practical Considerations When Building Anaerobic Digestors.

Solid retention time (SRT):

A key consideration when designing anaerobic digestors, that is often over looked is the retention of biomass in suspended growth reactors. The mean cell residence time (MCRT), also

known as the solids retention time (SRT) can be defined as the amount of time a bacterial cell will spend in the AD before being washed out [11], [17]. It is expressed as;

$$SRT = \frac{VX}{(Q - Q_w)X_e + Q_wX_R}$$

Equation 9: Equation used to define the solids retention time (SRT).

Where;

V is the reactor volume (L)

Q is the influent flow rate (L/day)

X is the concentration of biomass (gVSS/L)

Q_w is the flowrate of the wasted sludge (L/day)

X_e is the concentration of biomass in the effluent

X_R is the concentration of biomass in the activated sludge recycle line (gVSS/L)

The SRT is extremely important given the relatively slow doubling time of methanogenic bacteria. If short circuiting or a low SRT is present, the bacterial population in the digester will be severely affected as more bacteria will be lost from washout than is regenerated, impacting digester performance and eventually causing failure [12], [18].

Organic Loading Rate (OLR):

The organic loading rate (OLR) is defined as the total mass of substrate added per unit volume of the wastewater treatment process. It is expressed as;

$$OLR = \frac{Q * C_o}{V}$$

Equation 10: Expression of the organic loading rate.

Organic loading in anaerobic digestors is an extremely important concept as loading variations can upset the balance between the fermentation of organic acids and methane generation [11]. If not controlled properly, organic overloading can result in a rapid formation of VFAs (since acidogenesis is one of the fastest processes in AD) [11], [39]. The high concentration of organic

acids form will lower the reactor pH and potentially cause unfavourable conditions to methanogenic bacteria [11], [12], [17].

Alkalinity:

A common concern in operating AD units, which can have a substantial impact on the reactor performance and the operating costs, is the accumulation of volatile fatty acids (VFA). Anaerobic digestors are particularly susceptible to souring if the pH of the digester contents becomes too low (<6.8) [18]. The process of anaerobically digesting soluble organic molecules generates biogas bubbles containing carbon dioxide and methane [11], [12], [37]. The solubility of carbon dioxide in water to form carbonic acid reduces the pH of the reactor, becoming more acidic [11], [39]. Acidic environments are unfavourable to anaerobic bacteria which inhibit the metabolic function of methanogenic organisms [11].

[2.12 Case Study](#)

A practical demonstration of using an AD and an MBBR to pre-treat brewery wastewater before transfer to the municipal WWTP, has been demonstrated at the Spendrups Bryggeri AB, in Sweden. Spendrups is a large brewery which produced approximately 500,000m³ of beer per annum, and generates wastewater, with high concentrations of COD [40].

The brewery wastewater is heated before being fed into the AD, before MBBR treatment [40]. The MBBR unit after the AD process is to remove any excess organic material and to also remove methane and hydrogen sulfide from the AD process [40]. The AD and MBBR system is designed to achieve a COD reduction of 85%. It is also mentioned that after AD, the COD concentration of the supernatant are lower than the design load of the MBBR, this results in less COD removal from the MBBR process than designed for [40].

While success based on the desired aims has been achieved in Sweden, the same cannot be said to breweries in Australia. At the time of submission of this thesis, no known Australian brewery

has installed and successfully operated an AD +MBBR WWTP for effective management and treatment of brewery wastewater.

2.13 Identified Gaps in Current Literature

The gaps in current literature which have been identified are;

1. Limited knowledge on the effects of low temperature AD on brewery wastewater.
2. Unknown activation energy and reaction Arrhenius constants of AD of brewery wastewater.
3. The downstream effects on COD and TSS removal by pre-treating brewery wastewater anaerobically before aerobic treatment.

Chapter 3: Materials & Methodology.

A multistage and multidisciplinary engineering approach was adopted to address the aims and scope of this research project. This progression is illustrated in Table 7.

Table 7: Progression of research approach.

Phase	Description
I.	A review of existing literature was carried out to identify important points, the appropriate relationships between wastewater quality parameters, as well as identify areas of progress and areas where literature and data were limited in the contexts of anaerobic digestion of brewery wastewater.
II.	Baseline testing of the raw wastewater characteristics generated from the client's brewery was conducted, along with, baseline testing of the wastewater characteristics present within the existing moving bed biofilm reactor (MBBR) unit. This was done to establish a baseline of the quality of wastewater generated at the client's facility under standard operation.
III.	Design, fabrication and testing of a pilot scale anaerobic digester (AD) which would serve as the experimental platform for this study, factoring in information gathered during the literature review.
IV.	The experimental testing phase of the project focused on generating data, which would be used to address the scope of this project.
V.	A critically review of the results from the experimental testing process and establish appropriate advancements, limitations and determine a consensus for the outcome of this experiment. This will enable the validation or rejection of the project's hypothesis and allow for appropriate recommendations to the clients.
VI.	Assessment of the practical design considerations of a full scale system from the outcomes of this project.

3.1 Review of Existing Literature.

To model the performance of the AD and the MBBR unit, a thorough understanding of the various biological processes and wastewater relationships needed to be established. To do this, an initial review of current literature available was conducted.

3.2 Baseline Testing

The second step in this project was to establish an accurate baseline of the client's wastewater quality and the operational behaviours and characteristics of the MBBR unit currently installed. In addition to giving a clearer picture of the characteristics of the wastewater and the MBBR unit, baseline testing will aid in modelling different scenarios which the AD + MBBR system may encounter.

Baseline testing of the raw wastewater was conducted in the laboratory facility at Environmental Engineers International (EEI). Baseline testing of the wastewater being treated in the MBBR unit required on-site, in-situ testing at the client's brewery to prevent degradation of the wastewater samples. Testing of wastewater quality involved collecting samples and processing them via methods which are accepted via the AS/NZS 5667 Water Quality Sampling standards.

The key parameters tested in the raw wastewater were; COD, TSS, pH, TDS, ammonium, nitrate, nitrite, total nitrogen (TN), total phosphorus (TP) and orthophosphates. The methods used to analyse these parameters have been presented in Table 17, in Appendix B of this thesis.

COD analysis was preferred over BOD analysis as the results of the tests could be obtained in 2-3 hours versus 5 days respectively [41].

3.3 Anaerobic Digester (AD) Design and Fabrication.

This project was conducted as both a batch study (at 16°C and 30°C) and as an upflow pulse fed study (at 16°C, 20°C and 24°C) respectively. A batch study was conducted to determine the:

- A.** The total cumulative and daily volume of biogas which could be produced from the anaerobic digestion of brewery wastewater over time.
- B.** The maximum COD degradability of brewery wastewater.

A upflow pulse fed plug flow reactor (UPFR) study was conducted to assess:

- C.** The steady state daily biogas production at various hydraulic retention times (HRTs)
- D.** The steady state COD utilization of anaerobic digestion at different HRTs.
- E.** The steady state generation/destruction of TSS at different HRTs.
- F.** The net gain/loss of sludge based on the total organic load (total mass of COD over the duration of the study).

3.3.1 Batch Reactors.

Conical glass flasks with a working volume of 2L were used as batch reactors for this study. A total of 12 replicates were conducted at a temperature of 30°C, while two sets of experiments were conducted at 16°C. Each reactor was concluded when no observable biogas production was observed over 3 days.

The batch study was conducted at 30°C and at 16°C, representing a near optimal summer environment/heated environment and a sub-optimal winter-spring environment in Western Australia.

Biogas generated from the anaerobic digestion process was collected by displacing water in a filled and inverted measuring cylinder functioning as an eudiometer. The reactors were set up as per the process flow diagram (PFD) in Figure 12. Figure 13 represents the actual set up used for the batch studies.

Recording the daily volume of biogas generated using the eudiometer was used to address **(A)**. Initial and final total COD (COD_t) tests was used to address **(B)**.

3.3.1.1 Water Bath - Batch Reactor.

A 27L plastic container was used as the water bath for the study. The two conical reactors were submerged into the water bath, which was heated using an AquaOne 150L aquarium heater as the external heating element - Figure 13. The water bath temperature was maintained at 30°C

$\pm 1^{\circ}\text{C}$. The research space used which contained a heating, cooling and ventilation system maintained the ambient temperature of the space at $16^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

3.3.1.2 Biogas Collection System - Batch Reactor.

As stated earlier, biogas from the anaerobic digestion of brewery wastewater was measured via water displacement in a filled, inverted graded measuring cylinder - Figure 14. As biogas was generated, it would collect within the reactor until the pressure within the reactor exceeded the pressure needed to displace the water present in the inverted measuring cylinder. This is indicated by yellow arrows in Figure 14.

3.3.1.3 Reactor Seeding & Biomass Accumulation - Batch Reactor.

The anaerobic reactors used in the batch study was seeded using sludge obtained from an anaerobic lagoon, owned by a local abattoir and operated by EEI. An initial concentration of 10% (200ml) sludge to 90% (1800ml) brewery wastewater was used to cultivate biomass within the anaerobic reactor over an initial period of 28 days.

During the experiment, anaerobic sludge and biomass was retained in the batch reactors by allowing the reactor contents to settle, and then carefully decanting the supernatant and refilling the reactor with fresh wastewater for the following experiment.

3.3.1.4 Experimental Testing - Batch Reactor.

12 replicates were conducted over 5 months of testing for the batch study at a temperature of 30°C and 2 replicates were conducted at 16°C . A control reactor containing only anaerobic sludge was operated to evaluate the contribution of biogas from the sludge.

The reactor supernatant was then carefully decanted, where the sludge present in each of the reactors was retained and reused.

COD concentrations, sludge volume, pH and TDS were recorded at the start and end of each experiment, while biogas production was logged daily.

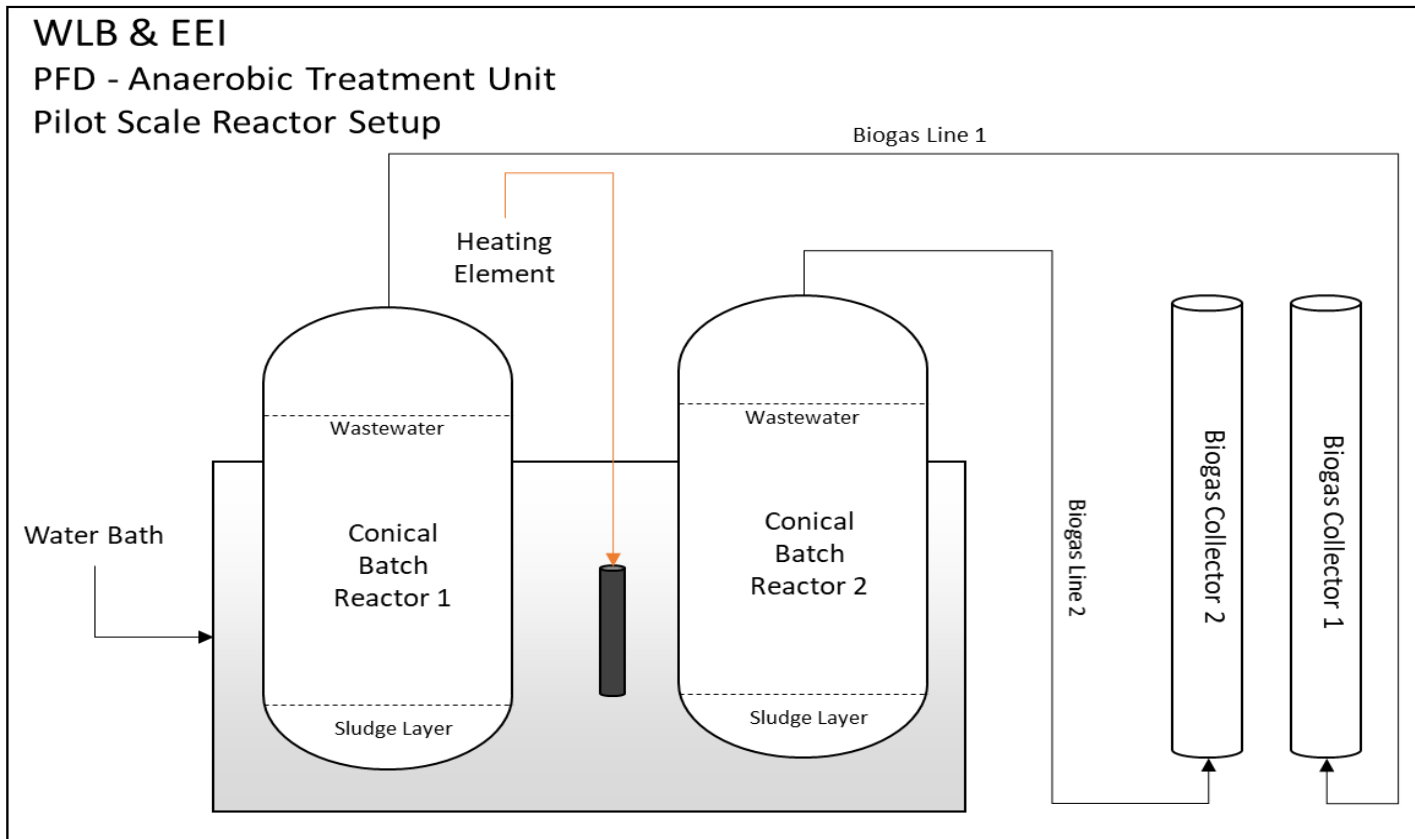


Figure 12: Batch reactor PFD.

Reactor Specifications:

- | | | |
|------|-------------------------|------------------------------|
| i. | Total Reactor Volume – | 2.5L |
| ii. | Reactor Wet Volume – | 2L |
| iii. | Reactor Walls – | Glass |
| iv. | Biogas Line Material – | 8mm silicone tubing. |
| v. | Heating Element - | AquaOne 150L Aquarium Heater |
| vi. | Water Bath Temperature- | 30°C ± 1°C |

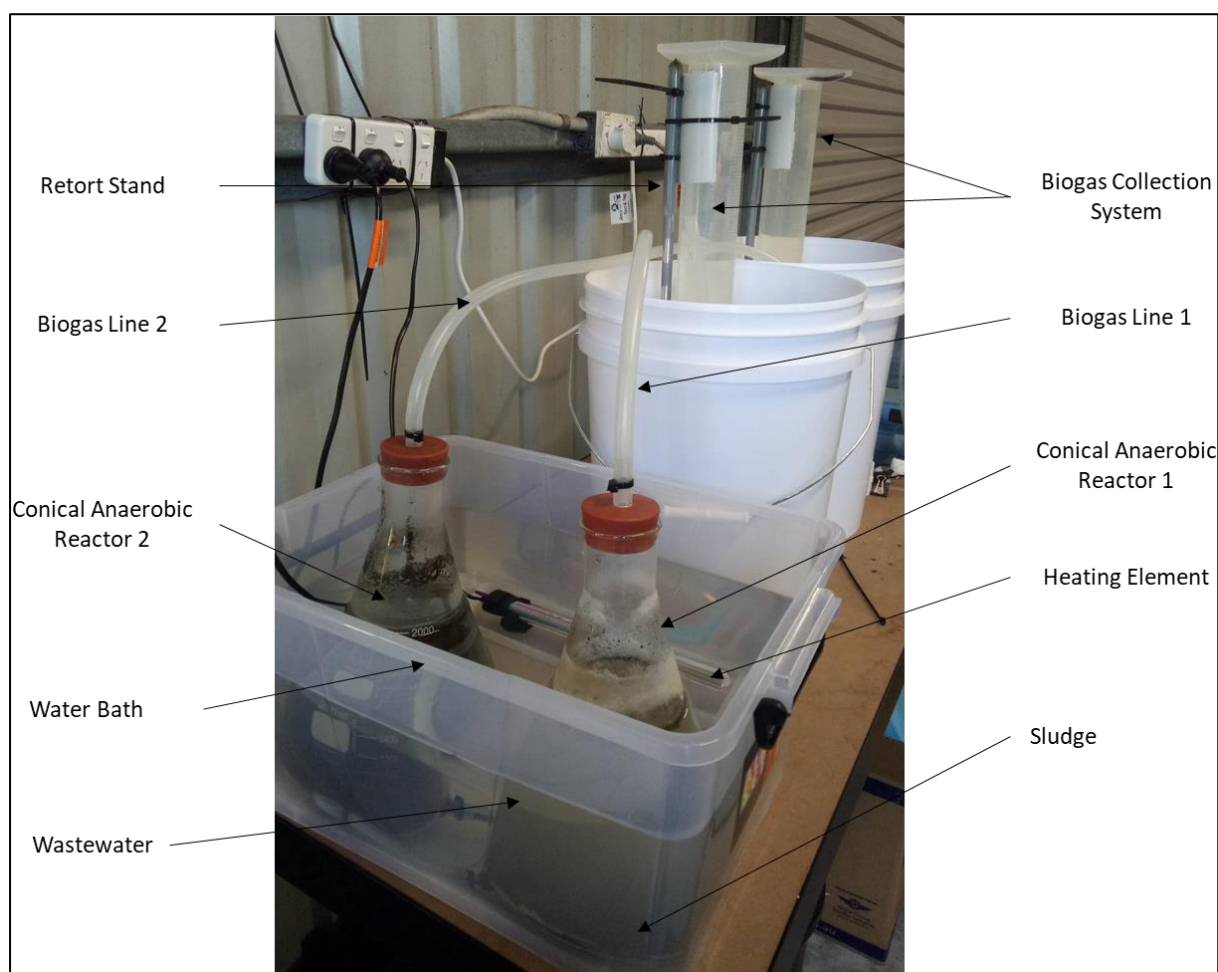


Figure 13: Illustration of the batch reactor used for this experiment



Figure 14: Batch study experimental set up and biogas collection method.

3.3.2 Anaerobic Upflow Pulse Fed Reactors (UPFR).

As briefly mentioned earlier, this project was also conducted as a pulse fed, up flow study. Recording the daily volume of biogas generated under a steady feed rate and HRT, will be used to address (C). Soluble COD (CODs) testing and TSS testing of the influent and effluent streams at various HRTs will be used to address (D) and (E) respectively. By emptying the reactor contents, the total volume of sludge generated/destroyed can be measured, allowing (F) to be addressed. While the system is technically pulse fed, Brownian motion, temperature assisted diffusion and structure of the reactor causes the reactor contents to continuously move. It is for this reason, this system is not a true plug flow reactor which is the rationale being modelling the system under continuous conditions and assumptions.

The purchase of a commercially manufactured anaerobic reactor for this pilot study was considered at the start of this project. However, several quotes placed the cost of purchasing a pilot scale anaerobic reactor between AUD\$2,000 and AUD 8,000 which exceeded the allocated project budget. Due to this, the anaerobic reactors were designed and built in-house. The anaerobic reactor units were designed and conceptualised using a PFD and 3-D modelling software (Google – SketchUp 2018, ANSYS R19.2 Academic 2018) represented in Figure 15 and Figure 16 respectively. Some modifications to the materials purchased were needed prior to installation. The completed anaerobic unit is presented in Figure 17. Each component used was safety tested before use.

The two plug flow reactors were operated at a temperature of 20°C, 22°C and 24°C. The wastewater feed was heated to a constant temperature of 34°C before it was fed into the anaerobic reactors.

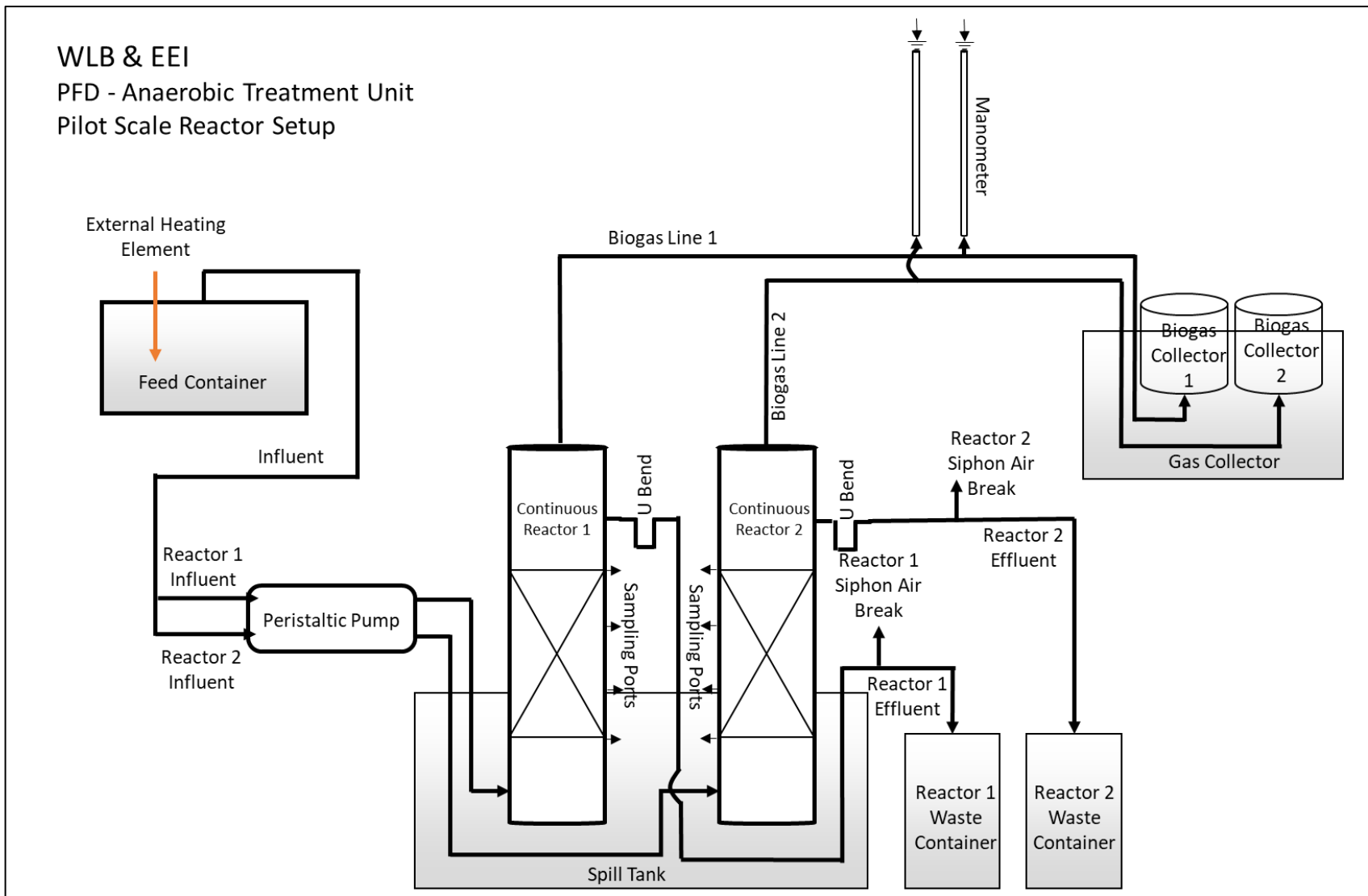


Figure 15: Pilot scale UPFR process flow diagram.

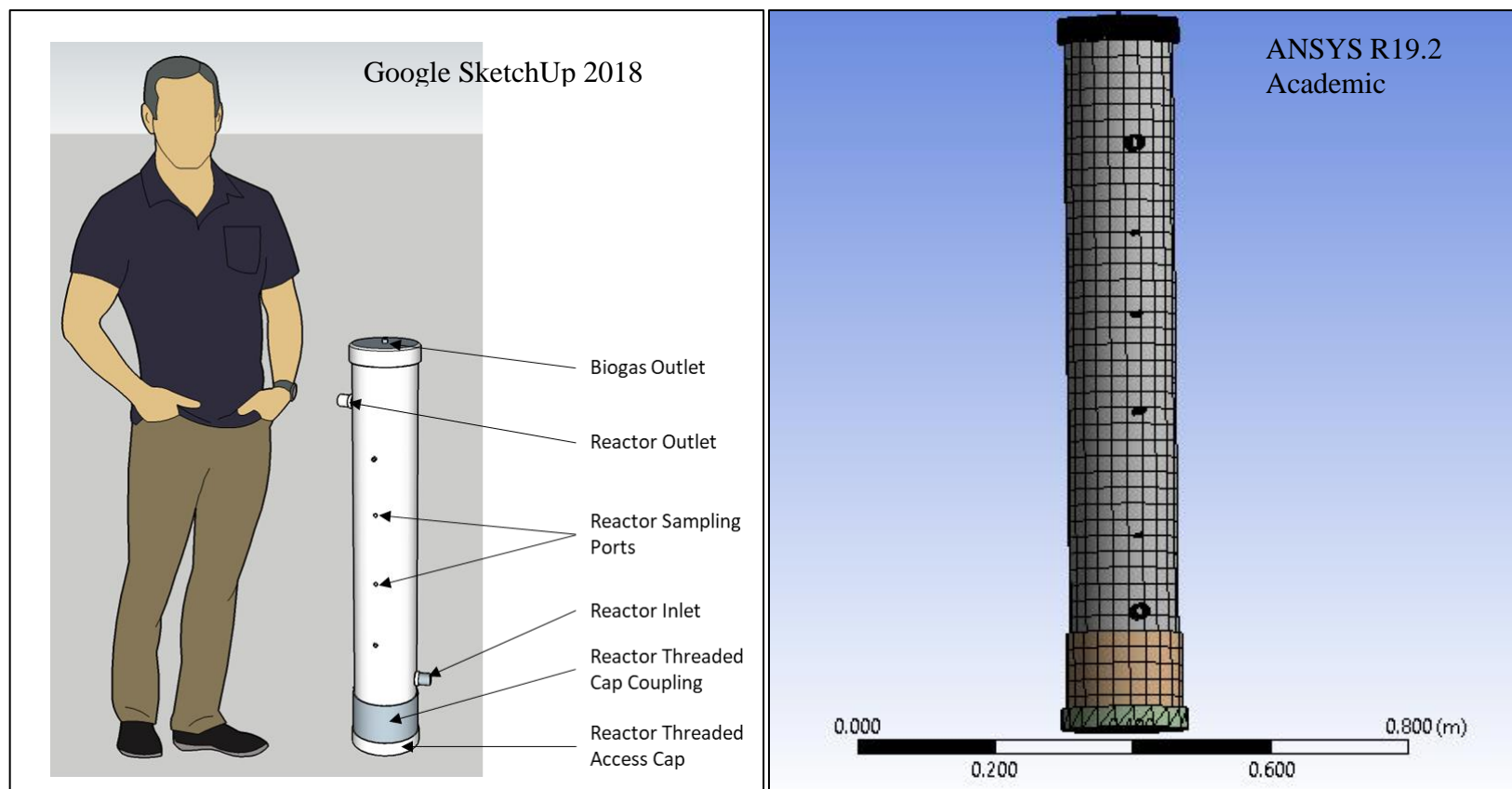


Figure 16:3-D full scale conceptualisation of the anaerobic reactor designed for the pulse fed continuous study.

Reactor Specifications:

i.	Total Reactor Volume –	17L	v.	Feed Heating Element -	AquaOne 150L
ii.	Reactor Working Volume –	15L		Aquarium Heater	
iii.	Reactor Walls –	3mm thick - PVC	vi.	Feed Temperature -	34°C ± 2°C
	DWV tubing		vii.	Inlet & Outlet Materials -	Combination of silicon
iv.	Biogas Line Material –	4mm silicone tubing.		and vinyl tubing.	



Figure 17: Completed UPFR anaerobic treatment unit.

3.2.1 UPFR Seeding and Biomass Accumulation

Both UPFRs were seeded using a 3:1 wastewater to sludge ratio. 5L of anaerobic sludge was fed into each reactor followed by 10L of brewery wastewater. Heated brewery wastewater was then fed at a rate of 3L per day for 6 weeks to enable the cultivation of biomass within each reactor as well as stabilisation of operating conditions. The HRT associated with the feed rate above was determined to be appropriate as the MCRT of the system was greater than the doubling rate of the methanogenic bacteria.

Reactor biomass was retained using a gravity system where any entrained biomass from the base of the reactor was given a sufficient height to settle to the reactor base without being syphoned out from the outlet. Several literature sources identified that the biogas formed would surround and adhere to the sludge particles causing some particles to rise to the reactor surface, before the biogas would detach from the sludge particles and settle [11], [12]. To prevent washout by removing sludge which had floated due to the buoyancy excreted by the biogas, the supernatant was removed from the reactor from a level (15cm) below the contents surface. These concepts are illustrated in Figure 18.

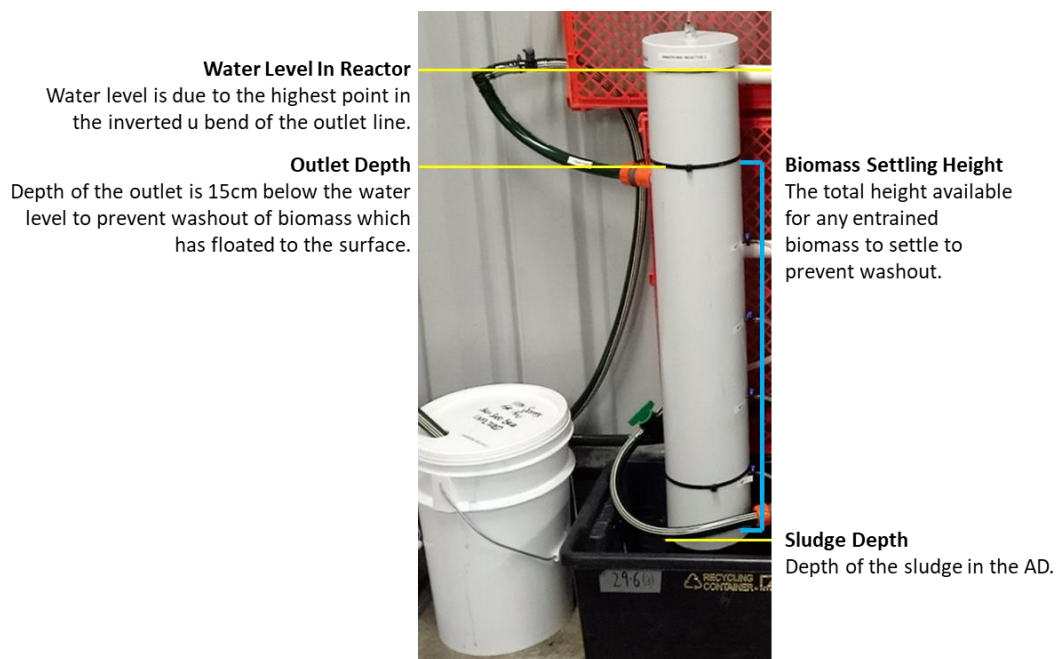


Figure 18: Biomass retention mechanism and washout mitigation strategy.

3.2.3 Experimental Testing - UPFR.

The UPFR study was designed to simulate the efficiency and performance of an actual AD unit implemented at the client's facility in COD and TSS removal. To do this, raw brewery wastewater was pumped into the reactor at different volumes to increase or decrease the HRT of the raw wastewater. The reactors were tested to ensure both systems were performing near identically, before one reactor was insulated using thick cotton towels and bubble wrap - Figure 19. Insulating one of the anaerobic reactors allowed a direct comparison of the role which temperature has on COD and TSS removal rates and biogas production rate.



Figure 19: Reactor 2 post installation of insulating medium.

COD testing of the influent wastewater (raw brewery wastewater), the wastewater at different sampling ports, along with the effluent (treated wastewater) would provide sufficient data to model the degradation of COD in the AD unit. In addition to this, the daily volume of biogas produced at different HRTs could be used to model the added by-product value of the biogas produced as well as close the overall mass balance of the treatment system. This would provide

an indication of the operational performance of the anaerobic digestors being investigated. Biogas was collected using a lightweight graded plastic container which floated according to the amount of biogas collected, a system adapted from EEI's proprietary self-regulating suspended biogas collector (SSBC) design. Hydraulic retention times of 5 days to 1 day was simulated by feeding the reactors with varied volumes of brewery wastewater. From this, the COD and TSS generation at different HRTs, along with the daily biogas produced was recorded and modelled.

3.4 Data Computation & Study

The bulk of the data computation for this study was completed using Microsoft Excel, thermal loss assessments were carried out using a computational fluid dynamic (CFD) software (ANSYS). Other software used were Google SketchUp and Microsoft Suite.

3.5 Practical Applications.

Using the information gathered from both the batch and pulse fed studies, the payback period of this project could be assessed by comparing different cases based on the final reactor design. Specifically based on the size of the reactor, reactor material, if insulation or heating would be preferred, etc. Several cases with the lowest investment costs and the shortest pay back periods are presented.

Chapter 4: Results & Observations.

4.1 Raw Wastewater Characteristics.

To determine the quality of the wastewater under standard operations, baseline data of the raw wastewater was collected. Results from this indicated that the wastewater varied in both chemical and physical characteristics. Baseline characteristics of the wastewater also indicated that up to 95% of the COD_t concentration existed as CODs. This high ratio is supported by several other studies [3], [16]. On one rare occasion, the CODs in the wastewater only accounted for <35% of the COD_t, this was the result of a rare operational issue upstream which caused significant quantities of suspended solids (SS) to migrate downstream. Such an event was only observed once and considered a one-off event and omitted from this study. Characteristics of the raw wastewater has been presented in Table 8 below.

Table 8: Raw brewery wastewater quality values obtained from baseline testing.

Raw Brewery Wastewater Baseline Characteristics					
S. No	Wastewater Parameter	Units	This Study Average	This Study Standard Deviation	Number of Samples Tested
1.	COD _t	mg/L	1654.7	588.5	30
2.	CODs	mg/L	1700.3	519	30
3.	pH	-	6.7	0.5	30
4.	Ammonium	mg/l	3.9	0.7	30
5.	Nitrate	mg/l	3.9	0.6	10
6.	Nitrite	mg/l	0.2	0.1	7
7.	TP	mg/l	18.5	7.1	7
8.	TN	mg/l	23.2	10.8	7
9.	Orthophosphate	mg/l	22.1	6.3	7
10.	(SPC) Conductivity	µs/cm	1357.3	543.5	30
11.	TDS	g/L	0.9	0.4	30
12.	TSS	mg/L	235.5	100.3	9

The high variability in wastewater quality makes establishing a standard baseline value difficult, as the results from one wastewater sample will not be representative of another. In addition to this, the high variability of the wastewater will make evaluating the overall mass balance of the system imprecise.

4.2 MBBR Operations.

To determine the operating baseline of the MBBR unit with respect to COD removal and TSS generation, wastewater from different points in the reactor were analysed. The table below represents the mean operational characteristics of the MBBR unit.

Table 9: MBBR baseline data collected.

MBBR Unit Average									
S.No	Parameters	Units	Raw Wastewater	Chamber 1	Chamber 2	Chamber 3	Chamber 4	Product Tank	Number of samples (n)
1.	CODs	mg/L	1654.7	823	451	422	57	<5	7
2.	Temperature	°C	17	17.13	17.13	17.15	17.10	N.D	7
4.	Conductivity	(μS/cm)	1357.3	955.5	973.0	973.0	954.0	277	7
5.	pH		6.7	8.30	8.26	8.25	8.23	7.2	7
8.	Ammonium	(mg/L)	3.9	2.17	2.23	2.11	2.18	N.D	7
9.	Nitrate	(mg/L)	3.9	1.81	1.90	2.38	1.95	-	7
11	TDS	(g/L)	0.9	0.62	0.63	0.63	0.62	0.18	7
12	Nitrite	(mg/L)	0.2	0.76	0.41	0.38	0.39	-	5
13	Orthophosphate (Ortho-P)	(mg/L)	22.1	26.17	29.13	25.90	14.73	<0.2	5
14	TN	(mg/L)	23.2	46.00	38.33	45.00	16.33	0.7	6
15	TP	(mg/L)	18.5	37.87	31.67	37.73	7.50	0.27	6
16	TSS	(mg/L)	235.56	2520	2237.5	2110	87.50	N.D	4

N.D – Not Detected

On average, 96.5% of the COD in the raw wastewater was removed by the MBBR unit, with the greatest reduction being observed between chamber 1 and 2. There was a 1068% increase

in TSS concentrations between the raw wastewater and the wastewater present in the MBBR unit. This large increase is likely due to SS in the form of sludge already being present in the reactor, from degradation of previous organics. What is interesting to note is that TSS concentrations in the MBBR unit reduce sequentially by 1.13% between chambers 1 and 2, and 0.94% between chambers 2 and 3. The large reduction in SS was observed between chambers 3 and 4 (95.9%), was due to the operating characteristics of chamber 4 (no aeration or agitation), allowing any SS transferred from chamber 3 to settle. While chamber 4 was expected to have no SS present in the supernatant, the extremely low HRT (< than 10 mins) of the MBBR unit likely prevents the SS from fully settling or entrains some of the settled sludge.

4.3 Batch Reactor Results.

4.3.1 COD Results.

Results from this batch study evaluating the biodegradability of brewery wastewater through anaerobic digestion at different temperatures indicated that on average 75% of the COD present in the wastewater could be removed by AD at 30°C, however only 63% could be removed at 16°C over 18 days. This indicates that temperature plays a statistically significant role in the anaerobic digestion of brewery wastewater. While several studies conducted on anaerobic digestion in thermophilic conditions indicate that it is possible to increase the performance in COD removal at higher temperatures, the energy demand of maintaining such a reactor temperature would render the economic viability of this project less than ideal. In addition, for denitrification to occur in the MBBR, COD is needed as the electron donor to facilitate the process [34]. As such, excess removal of COD via AD can likely cause issues downstream. It is for this reason, analysis on higher temperatures (>30°C) was not pursued. The temperature of the AD system varied by as much as 2 degrees Celsius, likely due to the thermostatic functions of the heating elements. AD system temperature was measured via an alcohol based

analogue thermometer. The error bars produced in Figure 20 represents the standard deviation of the % of COD removal.

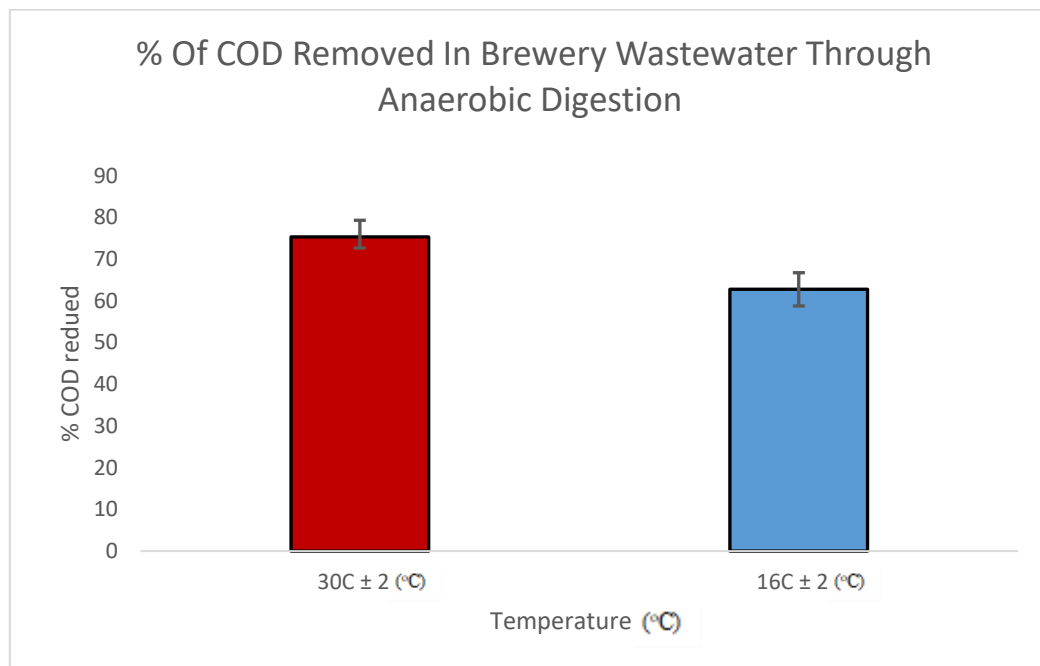


Figure 20: COD removal of brewery wastewater at different temperatures via anaerobic digestion.

Figure 20 represents the average removal of COD from a collective total of 14 replicates, (12 replicates from the 30°C system and 2 replicates from the 16°C). During this study, one replicate for the batch AD of brewery wastewater at 30°C failed and recorded no production of biogas. Biogas was not collected due to an operational issue in the experiment which likely contributed to the reactor failure – discussed in Chapter 5.

4.3.2 TSS Results.

TSS removal could not be assessed in the batch study due to the experimental set-up used. As TSS can only be measured by removing a sample from the reactor and drying it at 105°C, the introduction of air to the system would affect the results of the experiment. As such TSS data was not gathered for this experiment.

The closest approximation to the TSS generation in the batch AD reactors comes from the difference between the volume of seeded sludge at the start of the experiment and the volume

of sludge post experiment. Using the difference between the two volumes it is possible to approximate the amount of sludge generated. However, in practice this is not done for several reasons. The first is, without the known sludge density, the mass of the sludge cannot be determined. Secondly and more importantly, the apparent sludge volume can be affected by several factors such as the effect of compression (from the settling time) and even the F:M ratio, which affects the aggregate size of the sludge flocs [24].

4.3.3 Biogas Production.

AD at 30°C yielded a greater volume of biogas than AD at 16°C. This trend was apparent in all the replicates conducted. However, the volume of biogas produced in each replicate varied significantly. The figure below illustrates the mean volume of biogas produced at 30°C and 16°C. One outlying data set during the batch AD of brewery wastewater at 30°C, produced 30% more biogas than the other replicates. As this result was not replicated in any of the other batch reactors, it was omitted from the mean volume of biogas produced.

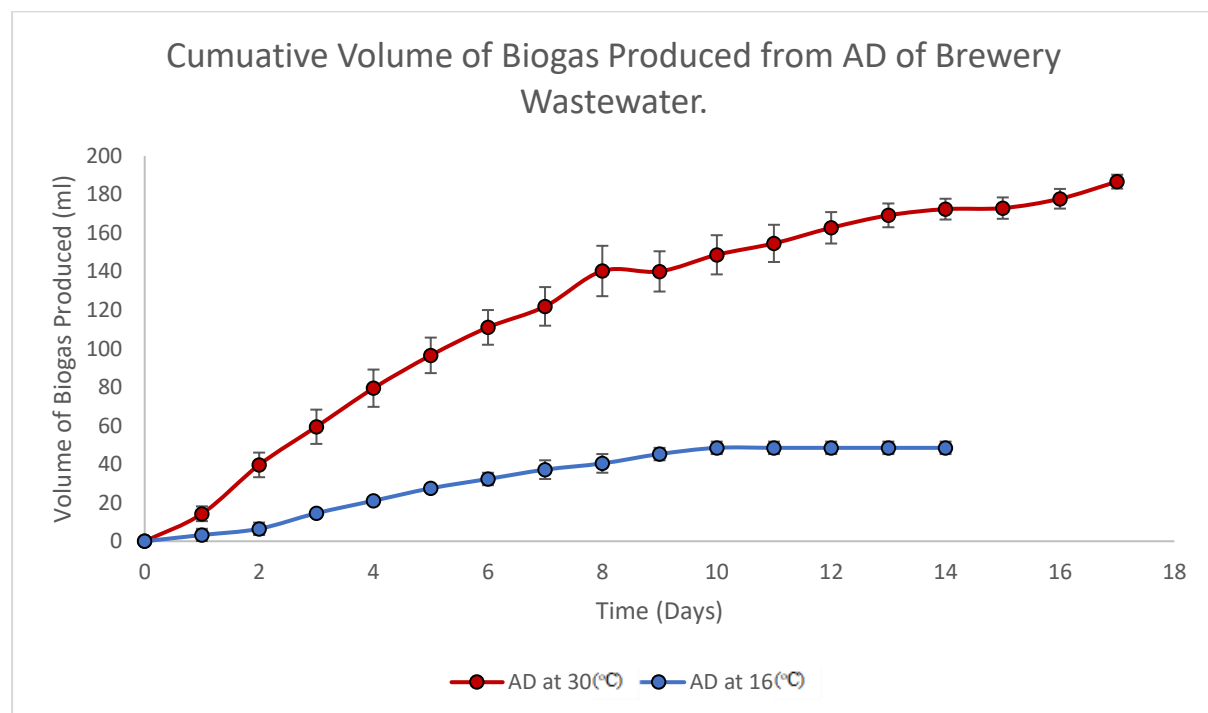


Figure 21: Comparative plots of biogas production at different temperatures.

At higher temperatures, AD of brewery wastewater produced more biogas than at lower temperatures, 187ml of biogas per gram of COD_t removed versus 48.5ml of biogas per gram of COD_t removed respectively. A possible reason for this difference could be the effect of temperature on the solubility of the different components of the biogas. The effect of gas solubility with increasing temperature is investigated further in Chapter 5.

The figure above also indicates that a greater standard error was observed from this study at 30°C than at 16°C. The errors observed are likely associated to the characteristics of raw wastewater used between samples, the fraction of CODs to COD_t present in the wastewater and surrounding environmental conditions. As anaerobic bacteria are only able to utilize COD in the form of CODs, the differences in biogas production may be attributed to the reduced rate of hydrolysis of complex organics into soluble organic and the slower metabolic activity of methanogens at lower temperatures.

In addition to this, preliminary observations indicate that the cumulative volume of biogas produced was significantly lower than the expected volume. An assumption was made that the wastewater contained only ethanol in the form of waste beer, to determine the maximum possible theoretical biogas generation volume. Only 40% and 10% of the expected theoretical value for the reactor at 30°C and 16°C was produced respectively. This variance between expected and theoretical volumes can be due to several factors such as leaks, the CODs to COD_t ratio, etc. This is discussed further in Chapter 5.

Another parameter which is crucial for modelling the production of biogas is the maximum biogas production rate (R_b) of the waste stream. Determining the maximum biogas production rate is a critical factor when modelling the cumulative volume of biogas produced.

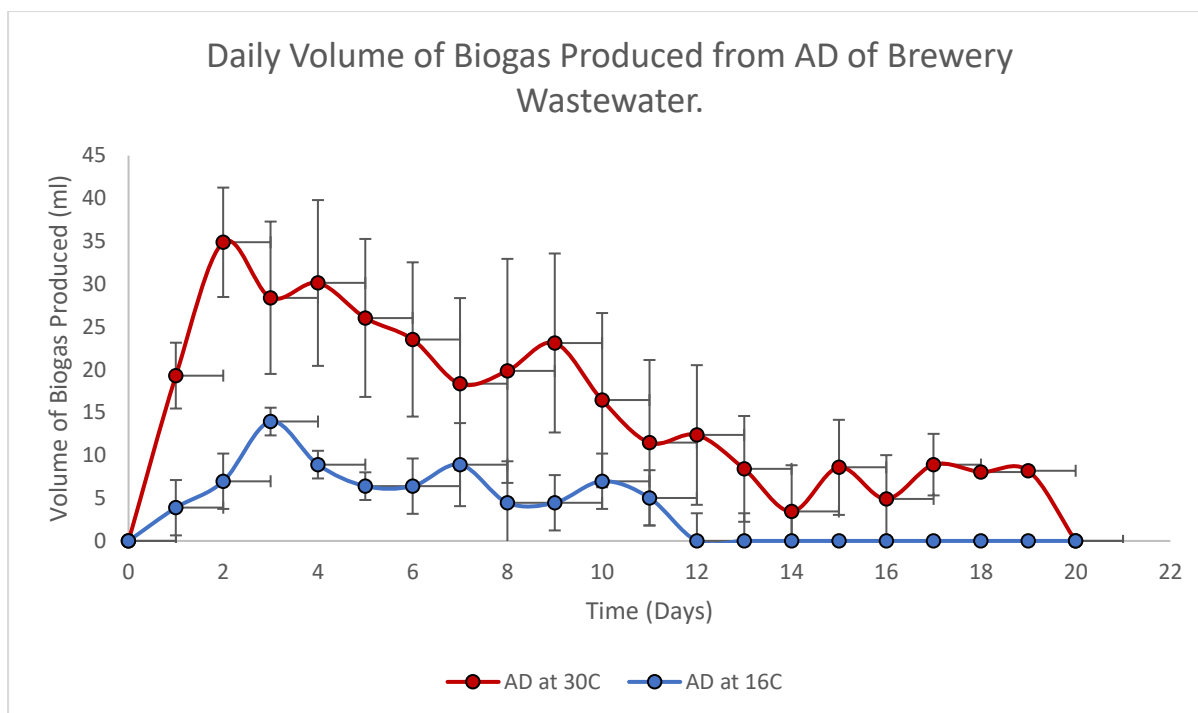


Figure 22: Daily volume of biogas produced over time.

Analysis of the daily volume of biogas produced, yielded a similar temperature trend as observed in the cumulative biogas production and the COD removal plots (Figure 20 and Figure 21). Daily volume of biogas generated also yielded a R_b value of 35ml and 14ml of biogas per gram of COD removed per day at 30°C and 16°C respectively.

In addition to this, both plots indicate that the greatest volume of biogas generated occurred in the first 7 to 9 days of introducing feed. This provides a crude estimate of the minimum HRT required to achieve near maximum CODs removal without operating the digester over a unnecessarily prolonged duration.

4.3.4 Reactor pH

A reduction in the pH between the raw wastewater (pH = 7.08) and the anaerobically digested wastewater was observed - Figure 36. Wastewater pH reduced by 0.58 and 0.31 for the digestors operating at 30°C and 16°C respectively. This is indicative of organic acids accumulation in the reactors. While it is unclear if temperature plays a significant role in the

accumulation of organic acids, preliminary results indicate this is the case, likely due to the temperature is a key contributory factor in reactor souring. Likely due to the metabolic activity of the acetogenic bacteria compared to the methanogens. However, as this was not present within the predefined scope of this experiment, this phenomenon was not investigated further.

4.3.5 Other Findings

Another experimental finding which were not considered in the scope of this project, included the effect of AD on TDS removal in the wastewater at different residence times. Results from this study indicate that up to 30% of the TDS present in the wastewater was removed at a HRT of 18 days -Appendix C, Figure 38. However, this was not investigated further.

4.4 UPFR Results.

4.4.1 COD Removal Results

To determine the optimal COD removal HRT, the up-flow anaerobic reactor was operated at a HRT of 5 days, 3 days and 1 day. Due to the characteristics of the wastewater stream, CODs was the preferred assessment parameter as it produced the most consistent data during testing.

To prevent the incorrect evaluation of the treated wastewater, the CODs of the effluent wastewater concentration was compared to the influent wastewater of that HRT +1 day for the wastewater to be removed from the system. For example, if the AD unit had a HRT of 5 days, the effluent CODs would be compared to the influent CODs 6 days prior. The reduction of COD at different HRTs has been presented below.

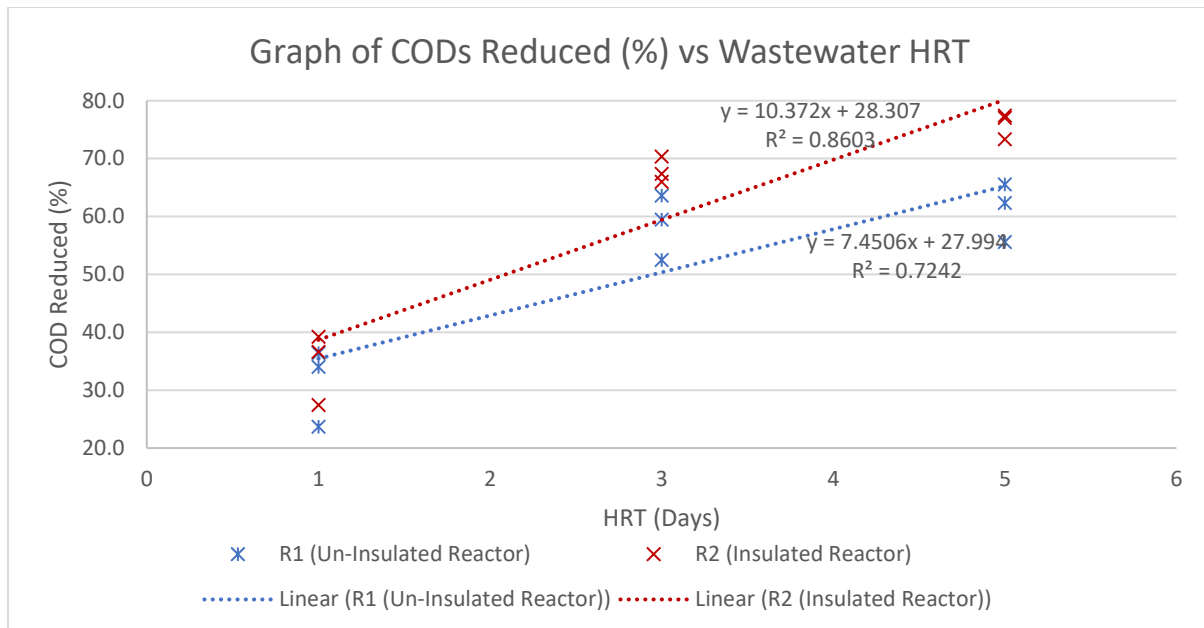


Figure 23: CODs removal at various HRTs.

From Figure 23, a directly proportional relationship can be observed between CODs removal and the HRT of the wastewater. In addition to this, the insulated reactor removed more CODs compared to the uninsulated reactor, supporting the results from the batch study.

The results from the UPFR study also indicate that a higher amount of CODs was removed from the insulated reactor operating at a HRT of 3 days than the uninsulated reactor operating at a HRT of 5 days. This indicates that insulation of the AD is likely more favourable compared to a longer HRT. This is a considerable factor when the practical and economic aspects of constructing the reactor is concerned.

A HRT of 1 day was observed to be the least effective in CODs removal, with a continuous decrease in reactor performance being observed. This along with an increase in COD_p in the effluent stream likely indicates that the biomass present in the reactor is being washed out.

The availability of biomass at different points in the upflow reactor was of particular practical interest as it can provide information regarding the appropriate sizing of the AD unit. The

relationship between CODs removal and the availability of biomass in the reactor at a 3-day HRT is presented below.

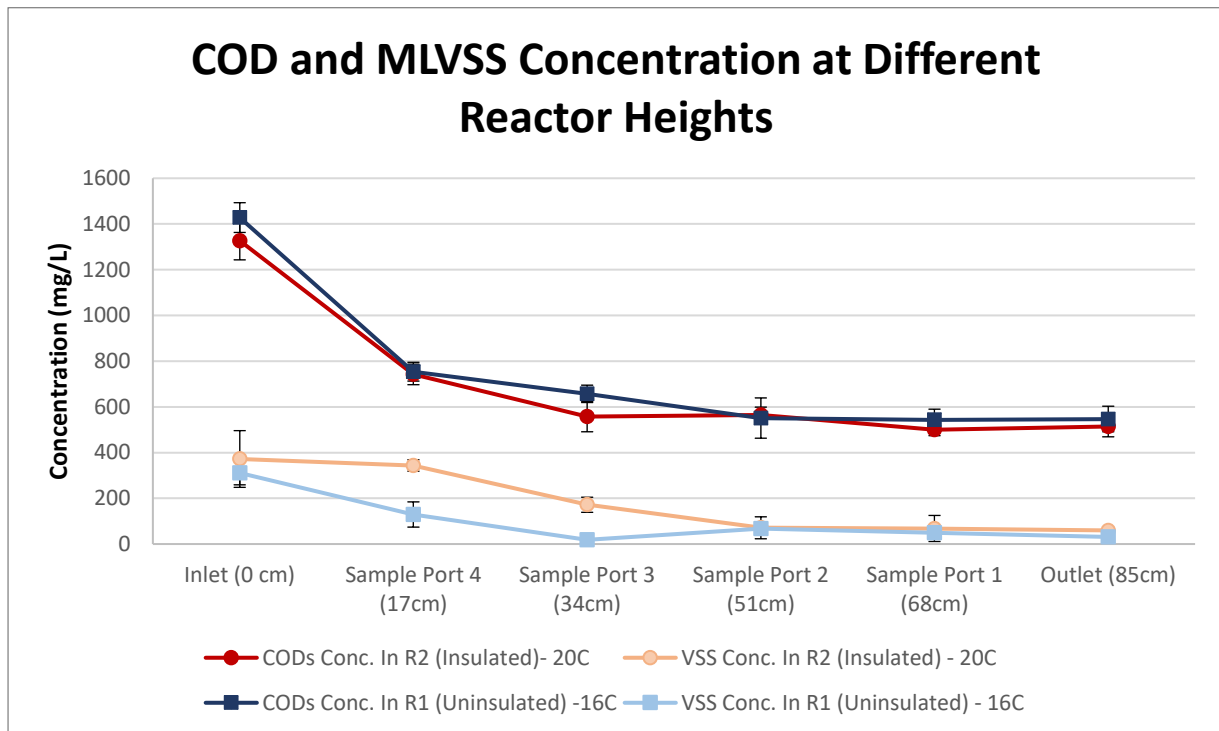


Figure 24: CODs and MLVSS concentrations at different heights along the AD operating at a HRT of 3 Days operating at 16°C and 20°C.

From Figure 24, up to 72% of the total CODs removed from the AD occurs in the first 34cm of the digestors, for both the insulated and uninsulated reactor. This indicates that even if the height of the AD is reduced, the COD removal will still be sufficiently high. The lowered height would translate to lower costs, at the expense of losing reactor volume should the AD unit serve as a wastewater storage facility also (as proposed by EEI).

The concentration of VSS on the other hand was observed to be higher near the supernatant surface. This is likely the effect of sludge particles being suspended in the region due to the buoyance force excreted by the biogas formation of the solid's surface, before the biogas bubbles detach. This should not affect the reactor design too greatly unless considering the available height of the reactor to prevent removing biomass. This can be overcome by installing

a sludge thickener or an anaerobic clarifier with a biomass return line. However, this will increase the capital costs and offset the savings made by reducing the reactor height.

4.4.2 TSS Reduction Results

Removal of SS present in the feed stream and the management of SS generated from the AD process are considered critical for this project. As mentioned earlier, the high concentration of TSS being generated in the MBBR unit can foul the UF membranes [5]. TSS can be generated from detritus material present within the anaerobic reactor system (even though this amount will be minimal since there is minimal assimilation in AD processes) or even from washed-out biomass/sludge. The figure below represents the percentage of TSS removed from the feed wastewater through AD.

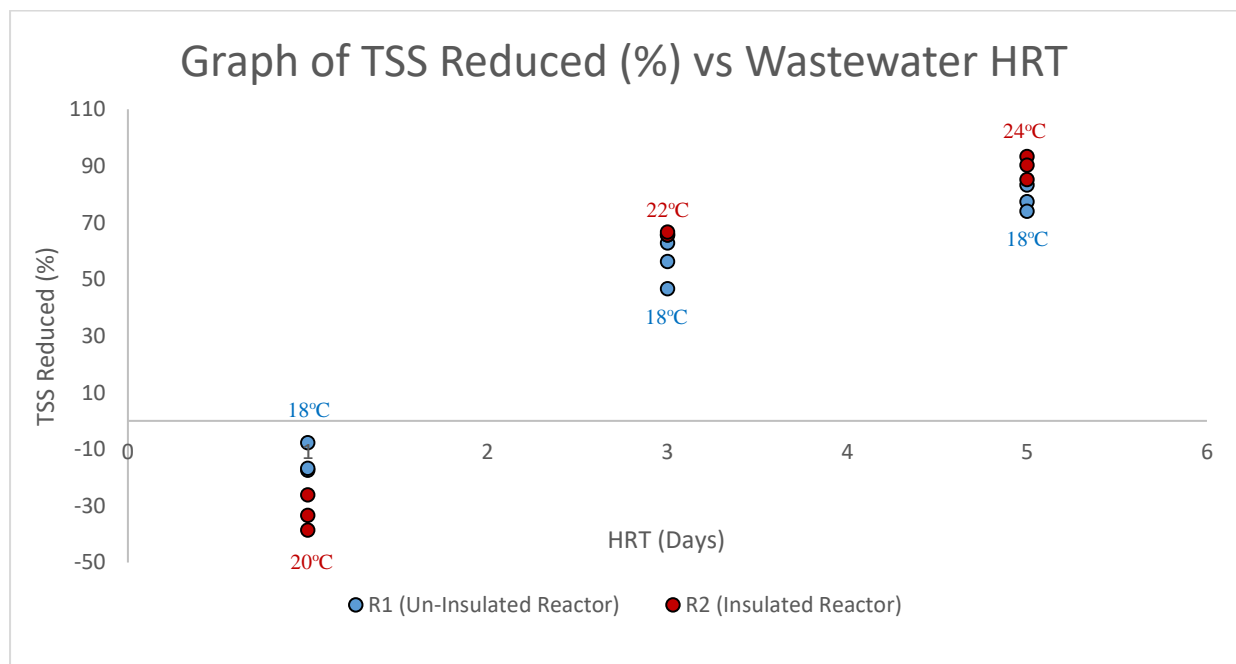


Figure 25: Removal of TSS in the UPFR system at various hydraulic retention times.

From the figure above, TSS removal was increased at higher HRTs, with the least removal of SS occurring at a HRT of 1 day. TSS testing of the influent and effluent wastewater post feeding indicates that 78% to 89.5% of TSS coming into the AD system can be reduced at a HRT of 5 days, and a temperature of 18°C and 20°C respectively. At a HRT of 3 day and 1 day, the percentage of TSS removal reduced to 55% to 60% and -14% to -32.5% respectively. The

negative removal values observed at a HRT of 1 day indicates that more SS is being removed from the reactors than is being fed. This indicates that there is significant loss of biomass in the form of sludge occurring. This would support the poorer CODs removal results at this HRT.

Aside from this, it can be seen that TSS removal did not vary greatly between the insulated and uninsulated reactors ($\approx 10\%$ difference), indicating that temperature did not affect the TSS removal as greatly as HRT did. From a practical design perspective this is an interesting result as the results from the TSS tests indicates that a larger reactor volume would be preferred over insulation.

4.4.3 Sludge Generation Results

A key focus of this project is the generation of sludge from the AD unit. High sludge generation in the MBBR unit is the attributed cause of fouling of the UF membranes. Thus, it is important that AD be able to provide a lower sludge generation than the MBBR unit. While sludge generation could not be quantified in the MBBR unit due to the size of the system, sludge generation will have to be compared to the expected sludge generation of aerobic systems (30%-60% of the organic load).

By determining the mass of sludge which accumulated in each reactor, and the total organic load which each reactor was subjected to, the mass of COD which was converted to sludge was determined. This has been presented below.

Table 10: Determination of the % of COD converted to sludge.

S.No	Name	Sludge Volume at Start of Experiment (ml)	Sludge Volume at End of Experiment (ml)	Net Sludge Volume Gain (ml)	Sludge Density (mg/ml)	Total Organic Load (mgCOD)	% COD Converted to Sludge
	Average	5000	5800	800	1400	245656	4.6

From Table 10, it can be seen that the AD operated for several months only converted 4.6% of the COD loaded in, into sludge, unlike aerobic systems which usually convert between 30% to 60% of the organic load to sludge. These results are lower than the predicted range of sludge generation of AD units (5% to 10%). That said, the volume of sludge retained in the reactor at the end of the experiment does not reflect the volume of sludge lost through washout over the course of this project, especially at a HRT of 1 day. Equipment constraints prevented the mass of sludge washed out of the reactor from being measured. While the duration of the experiment is substantial, it would be prudent to remember that the sample size verifying this result is also extremely small ($n=2$) and requires further testing to establish a definitive relationship and reduce the effects of any random outliers.

4.4.4 Biogas Production Results

It was proposed that the biogas generated from the AD process would be collected and used as a cooking gas alternative to the LPG gas that is currently used at the tavern.

To determine the add by value of the biogas generated from the AD unit, the volume of biogas produced each day was recorded. This was done in the hopes of establishing a steady baseline of biogas produced. However, this was harder than expected. Due to the design of the AD unit and the biogas pressure needed to overcome the pressure excreted by the gas collector the volume of biogas produced daily varied at different loading rates. In addition to this, the entrapment of biogas also contributed to the varied biogas production volume. A sample of the variability of the biogas generation data has been included in Appendix C of this thesis. To minimize the effect of this, the daily biogas produced was collected over 2-3 weeks and averaged to determine a daily volume of biogas production. The volume of biogas produce at each HRT has been presented below.

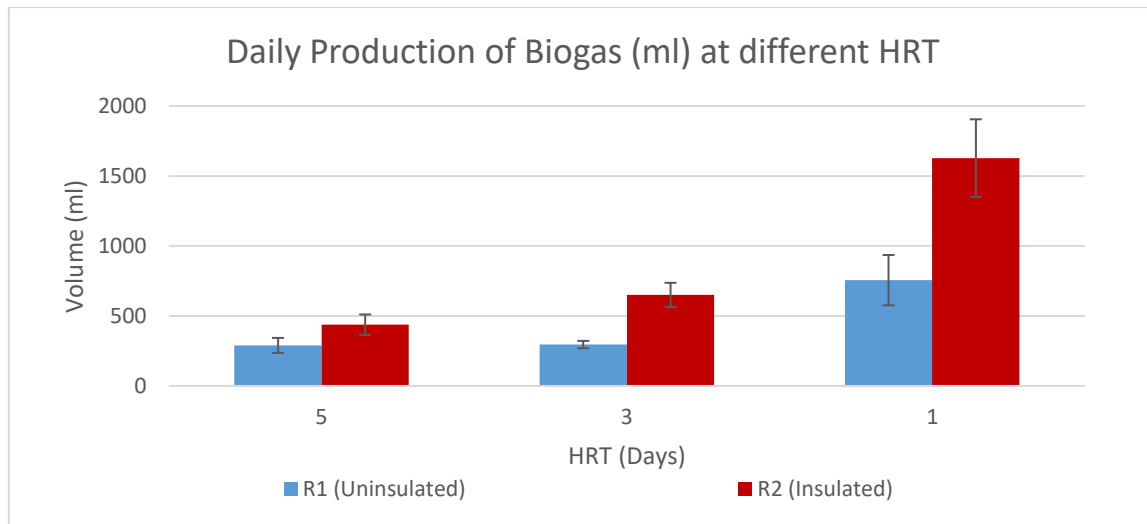


Figure 26: The average daily volume of biogas produced at different HRTs.

From Figure 26, it can be seen that the insulated reactor produced more biogas than the uninsulated reactor. As both systems were operating near identically, the difference in biogas produced suggests that the reactor temperature plays a significant role in the activity of the AD process. This is supported by the results from the batch study and the amount of COD removed from the wastewater. However, when the HRT of the wastewater was reduced to 1 day, and both reactors were subject to near identical operating temperatures of 24°C, more biogas was still produced from the insulated reactor compared to the uninsulated reactor. Only 46.6% of the volume of biogas produced in the insulated reactor was produced in the uninsulated reactor. This could possibly due to the lower concentrations of CODs removed from the wastewater and converted to biogas. In addition, the lower operating temperatures of the uninsulated reactor would have resulted in lower microbial activity, resulting in a lower conversion of COD to biogas.

Aside from this, the most important information which can be obtained from this plot is that the volume of biogas produced increased as the HRT of the wastewater and COD removal reduced. This is due to the increased organic loading rate (OLR) the reactor is subject to – discussed in Chapter 5. In addition to this, increasing the OLR above the reactor threshold can result in significant operational issues, discussed in Chapter 5.

Biogas Analysis

To evaluate the characteristics of the biogas generated, a limited number of biogas samples (n=3) was analysed for their composition using a gas chromatography thermal conductivity detector (GC-TCD). This method of analysis was chosen as it satisfied the requirements of assessing the ratio of methane to carbon dioxide in the sample. This method of biogas analysis has been used in before in a paper produced by Palandri, M in 2012 from the University of Western Australia. In addition, a similar method of analysis was also used to quantify gaseous emissions from anaerobic digesters for the UNFCCC by EEI in 2012. Ideally however, as the majority of the gasses produced during AD are ‘light gasses’ a Fourier-transform infrared spectroscope (FTIR) would be used to provide a more accurate determination of the individual gasses with respect to the overall composition of the biogas. However, as such equipment was not available at the time of this project and exceeded the project budget, a compromise was made. The results of the GC-TCD analysis has been presented below.

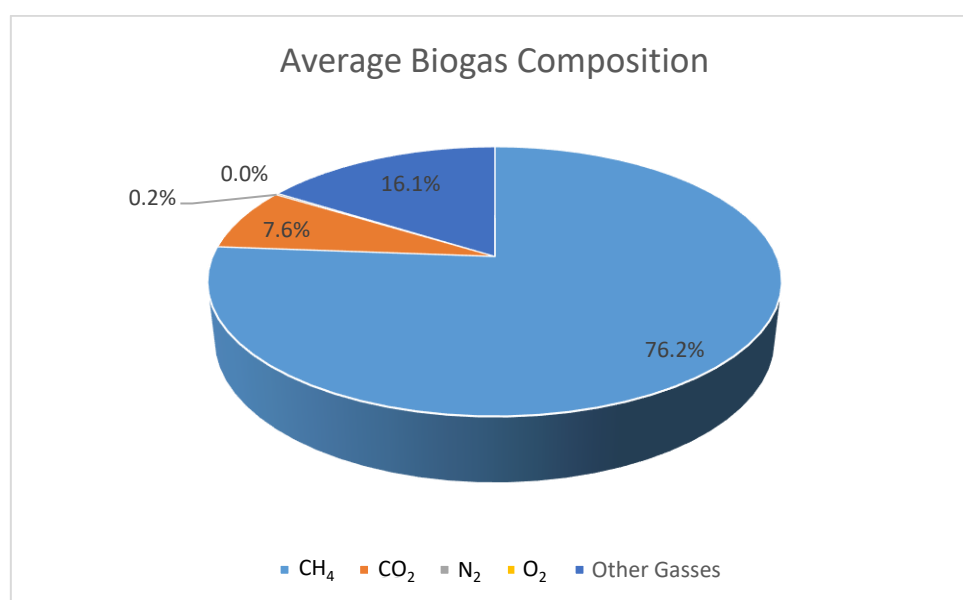


Figure 27: GC characterisation of biogas produced from the anaerobic digestion of brewery wastewater.

Results from the GC-TCD analysis indicated that the methane concentration in the tested biogas samples was higher than expected, 76%-76.4% v/v of the total gas contents. This was higher than literature sources which placed the average contribution of methane in biogas

between 55%-70% methane [18], which raises a few points of discussion. Carbon dioxide concentrations were subjected to the same issue as the methane concentration as they were significantly lower than expected (7.6%-7.5% v/v). Literature sources placed the average carbon dioxide composition of biogas between 30%-40% of the total gas volume [18].

Assuming that the wastewater stream was composed of only ethanol, these results did not balance via stoichiometry and indicated that the GC results did not reflect the ‘whole story’. This is discussed further in Chapter 5. However, similarly high CH₄ and low CO₂ fractions were observed in another study using a similar reactor design [42].

GC-TCD analysis indicated that a large component (15.9% - 16.2% v/v) of the biogas samples tested contained uncharacterised gasses. While the gas chromatography of the biogas sample was not able to identify the gasses, it is likely that these gasses are a mixture of water vapor, hydrogen, ammonia and nitrogen oxides [43]. GC analysis also indicated that there was no hydrogen sulfide present in the biogas.

4.4.5 Reactor pH Results

Reactor pH at HRT of 5 days and 3 days remained fairly constant between the un-insulated and insulated AD units, operating at an average pH of 7.24 and 7.30 respectively. No significant change in reactor pH was observed at HRTs of 5 days and 3 days. However, a drop-in reactor pH from 7.24 to 7.03 and 7.3 to 6.96 was noticed in both reactors at a HRT of 1 day respectively. The reduction in pH of both reactors combined with the higher concentration of COD_p in the AD effluent likely indicates that washout of biomass is resulting in a build-up of organic acid, consequently reducing the reactor pH. From a practical design and operational standpoint, the accumulation of organic acids has the potential to cause serious issues when the reactor is scaled up. In addition to this, these results also indicate that a full-scale system will require the addition of alkalinity.

4.4.6 Other Findings

A. Nutrient concentrations in the influent and effluent wastewater remained largely unchanged.

This supports finding from other studies which indicate that anaerobic digestion does not play significant consequence on nutrient removal.

B. Similar results to the batch study was identified in terms of TDS concentrations. Results from this study indicate that TDS concentrations in the treated wastewater was reduced by up to 12%. However, as this was outside the scope of this study, the reason for this is not investigated further.

Chapter 5: Discussion.

As mentioned at the start of this document, the primary aims of this project was to evaluate the COD and TSS degradability of the raw wastewater via AD, determine the reaction activation energy (E_a), the treatment Arrhenius constant (θ) and model the downstream effects of implementing such a system on the UF membranes in the WWTP.

5.1 Raw Wastewater Characteristics.

The baseline raw wastewater characteristics were highly varied, with significant variability observed in the COD and SS concentrations. This prevents the determination of an ‘average’ concentration as any estimate made would result in a significant error. This variability is also noted in several studies [3], [16].

Table 11: : Comparative raw brewery wastewater quality values obtained from this study versus other studies

Raw Brewery Wastewater Baseline Characteristics							
S. No	Wastewater Parameter	Units	This Study Average	This Study Standard Deviation	Number of Samples Tested	Literature Study 1 Average [3]	Literature Study 1 Standard Deviation [3]
1.	COD _t	mg/L	1654.7	588.5	30	5340.97	2265
2.	COD _s	mg/L	1700.3	519	30	3902.28	1644
3.	pH	-	6.7	0.5	30	6.0	1.44
4.	Ammonium	mg/l	3.9	0.7	30	8.62	10.40
5.	Nitrate	mg/l	3.9	0.6	10	4.30	3.41
6.	Nitrite	mg/l	0.2	0.1	7	0.37	0.18
7.	TP	mg/l	18.5	7.1	7	-	-
8.	TN	mg/l	23.2	10.8	7	5.36	
9.	Orthophosphate	mg/l	22.1	6.3	7	23.71	21.88
10.	(SPC) Conductivity	μs/cm	1357.3	543.5	30	1520	481
11.	TDS	g/L	0.9	0.4	30	-	-
12.	TSS	mg/L	235.5	100.3	9	1.8	0.97

To model the downstream effects of implementing the AD system at the brewery, the highest and lowest concentration of COD and TSS was used. This allows the effects of a higher and lower concentrated wastewater stream on the downstream processes to be evaluated.

While outside the scope of this study, the variability of the raw wastewater can be attributed to several factors such as; the volume of beer produced, the volume of water used in the facility or even the type of beer produced.

A key result in this baseline testing is the pH of the wastewater stream (6.7 ± 0.5). The acidic nature of the wastewater and the reduction in pH observed at a HRT of 1 day can pose several design and operational considerations, mainly:

The low pH of the wastewater coupled with VFAs formed during acidogenesis and the reaction of CO_2 (from methanogenesis) with the wastewater to form carbonic acid can lower the pH of the reactor to a level which causes souring and reactor failure [11]. To neutralize the low pH and increase the alkalinity, suitable chemical reagents need to be added to the reactors to maintain optimal operating pH, usually between 6.7 and 7.2 [44]

That said, lower pH levels in the raw wastewater can have a unintentional positive effect of particle destabilization. Most SS present in wastewater is negatively charged [11]. The presence of a wastewater stream with low pH indicates that there is an abundance of H^+ ions [45]. The positive nature of the hydrogen ions allows some binding and charge neutralization to occur between the surface of the negatively charged SS and the H^+ ion [11]. This destabilizes the particle making settling and coagulation easier due to the reduced repulsive electrostatic forces excited by the SS particle [11], [46].

Another aspect which needs to be actively considered is the toxicity of total ammonia nitrogen (TAN) to the anaerobic digestion process [47]. TAN can fraction into free ammonia nitrogen and ammonium nitrogen, each of which is inhibitory to the function of methanogenic bacteria

[48]. Decline in aceticlastic methanogens and hydrogenotrophic bacteria was observed when the concentration of ammonium in the waste stream was greater than 3g/L [47]. However, as the concentration of ammonium in the wastewater is low, ammonium/ammonia toxicity is considered unlikely.

5.2 MBBR Operations.

Operational results obtained from the MBBR unit indicate that the system is performing as designed, removing up to 96% of the COD present in the wastewater. As mentioned earlier, the generation of SS and removal of COD in chambers 1 to 3 was observed to reduced. The continuous reduction of SS observed in all 4 reactor chambers may either indicate that; the baffles installed between each chamber acts as a system which mitigates the transfer of sludge between chambers and/or (a more likely explanation) there is less biomass generated in each consecutive chamber. Practical design reports of MBBR systems indicate that COD utilization is the primary focus in the first MBBR chamber [11] with subsequent chambers are used as nitrification and denitrification phases [18]. This is done to reduce the available substrate and prevent space competition between the heterotrophic bacteria and nitrifying bacteria on the MBBR media [11].

5.2.1 Modelling COD Removal - MBBR

Substrate removal via attached growth processes mainly depend on a multitude of factors such as the characteristics of the biofilm and biomass [11]. Several mechanistic models have been developed to describe the biological substrate utilization rate and mass transfer in attached growth, biofilm processes [11], [49]. One method which has been widely accepted is the expression of organic substrate (COD) utilization using the Schulze equation [49]. However, as the accuracy of the model was unknown, the predicted effluent CODs concentrations were

compared to experimentally determined results - Figure 28. The Schulze expression for substrate utilization in biofilm processes has been presented below:

$$\frac{C_e}{C_o} = \exp(-K'DQ^{-n})$$

Equation 11: Schulze equation for the expression of substrate utilization in biofilm processes [49].

Where;

K' is the treatability factor $((L/s)^{0.5}/m^2)$ – assumed to be 1.3835 from previous brewery wastewater treatment study [50].

D is the filter depth (m) – between 0.9m and 1m (0.95m used in all calculations).

Q is the hydraulic load (L/s) – (15,000L/d max- at time of testing \approx 12000L/d) [4].

n is the constant characteristics of the media (assumed to be 0.5873) [50]

Other terms defined previously.

C_o is the initial (influent) wastewater COD concentration.

C_e is the effluent wastewater COD concentration

Rearranging Equation 11 and applying the average influent concentration which was determined during baseline testing (1654.7mg/L), we can calculate the predicted effluent concentration.

Compared to the actual concentration determined from testing (56.9mg/L), the model above is able to predict the effluent COD concentration of the MBBR process with moderate accuracy. The figure below compares the predicted effluent concentration from the Schulze model against the effluent concentrations determined from baseline testing.

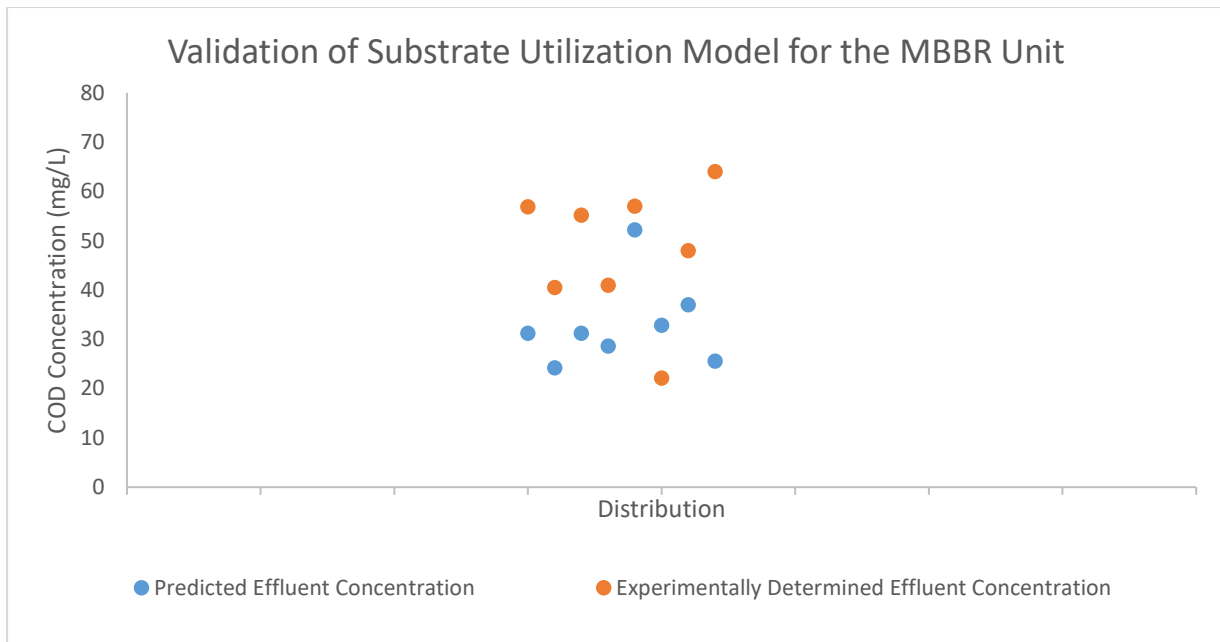


Figure 28: Validation of Schulze model for predicting the effluent substrate concentration of the MBBR currently in operation.

From Figure 28, it is seen that the Schulze model yields an effluent concentration which is slightly lower than the actual concentration determined from testing. This is most likely due to operational limitations of the model. In addition, as this model is derived empirically, the predicted output of the model above would more closely match outputs of the system this model was based upon.

5.2.2 Modelling TSS Generation - MBBR

TSS in the MBBR unit was modelled by developing a ratio between the influent CODs concentration and the TSS concentration present in each reactor chamber - Figure 29 and Figure 25. This relationship is known as the CODs:TSS conversion factor ($f_{cv,COD:TSS}$). This relationship is purely empirical and only reflects the system currently operating at the client's brewery. The conversion factor allows us to determine the concentration of TSS at any point in the MBBR unit.

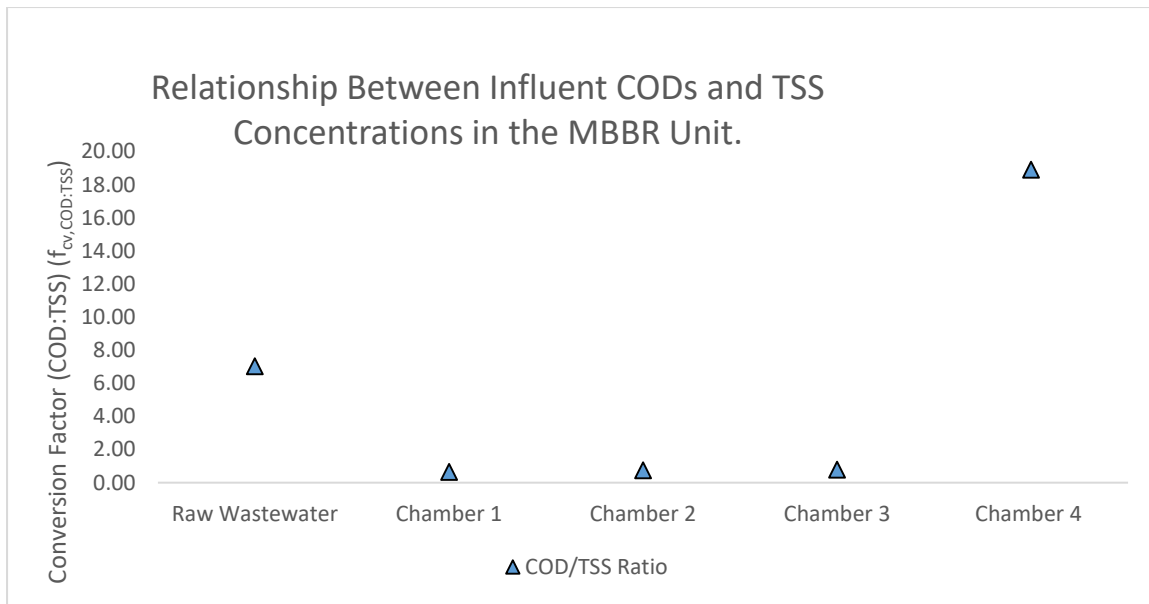


Figure 29: TSS concentrations present at each point in the MBBR treatment process.

The figure below represents the accuracy of the empirical model determined above in predicting the TSS concentrations at different points in the wastewater treatment process.

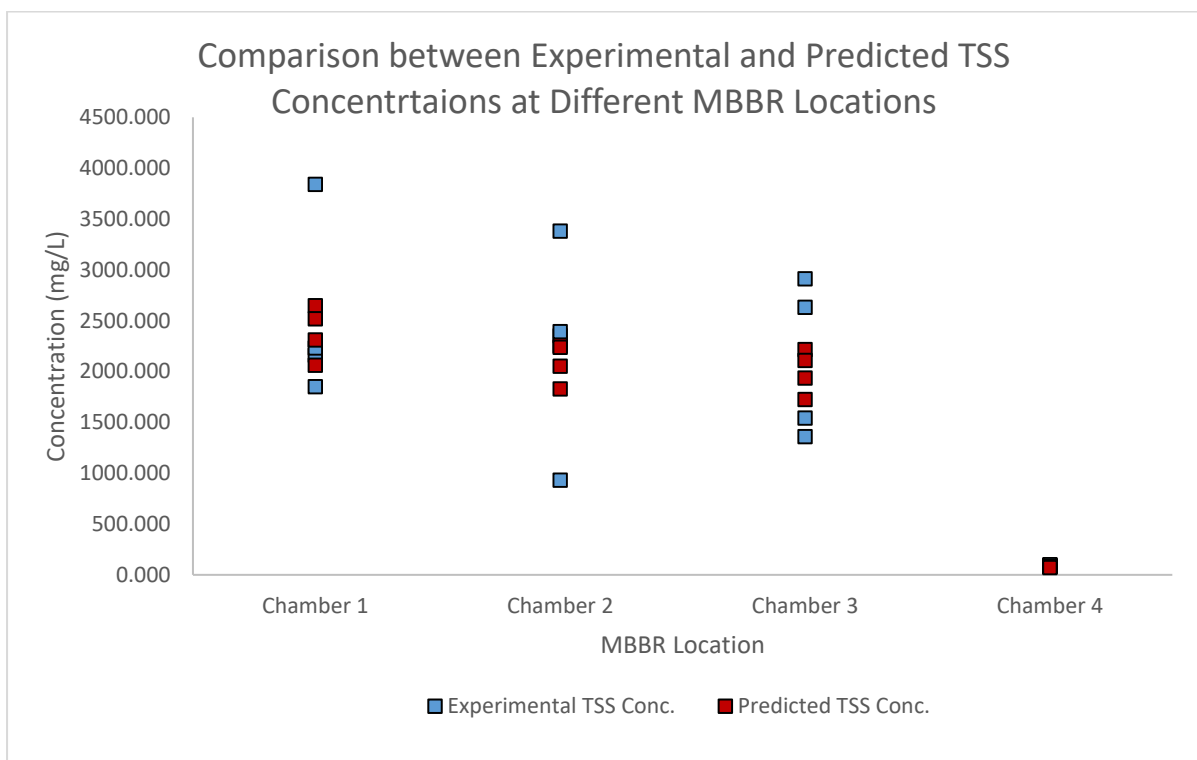


Figure 30: Validation of $f_{cv,COD:TSS}$ relationships compared to experimental data gathered.

The above model can be easily modified to accommodate the rate of TSS generation by replacing the influent COD concentrations with the OLR. The resultant solution would be the TSS generation per unit time.

5.3 Anaerobic Digestion as A Batch Process.

Due to the experimental design, daily COD concentrations could not be experimentally modelled. Once the environment inside the reactor is exposed to air, it no longer stays anaerobic. As such, COD consumption was modelled theoretically by establishing several assumptions, which were; 1. The COD utilization rate is directly proportional to the biogas production rate; 2. COD removed can only presents itself as biogas and sludge; 3. COD removed via precipitation or assimilation is considered negligible; 4. Raw wastewater composition is only ethanol from spent beer; 5. There is no COD_p present in the supernatant.

COD Mass Balance.

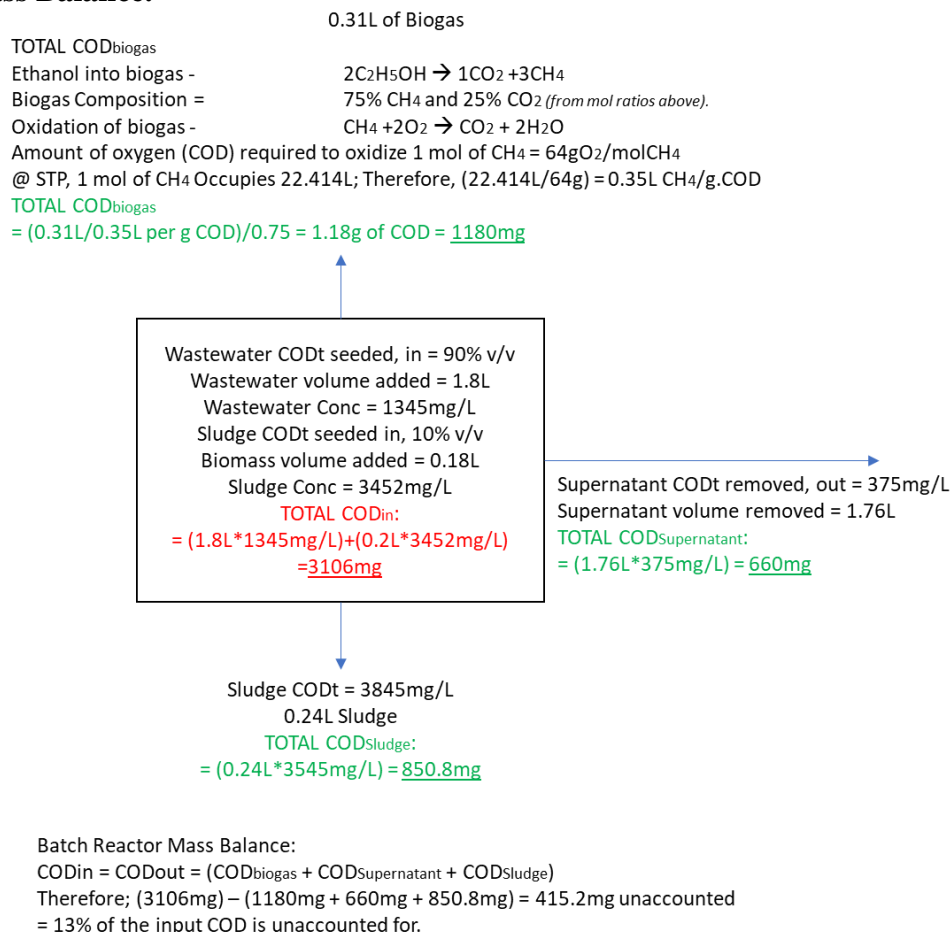


Figure 31: Batch reactor mass balance.

The percentage of COD unaccounted for in each replicate varied between 11.1% to as much as 47%. However, on average, in the 12 replicates conducted, the percentage of unaccounted COD was 31%. The COD which was not accounted for may have been removed as; COD_p in the

supernatant, as precipitated COD or even as dissolved CO₂ or methane in the supernatant. It is important to note that ethanol was used as a reference substance in the mass balance analysis as it is assumed to be representing the largest component of the wastewater stream (from spent beer) and is a product of the fermentation process.

5.3.1 COD Utilization Model – Batch Configuration

As the rate of COD utilization was dependent on the rate of biogas production based on the assumptions made, the utilization of COD was modelled using first order kinetics. This reflects the method used in other studies as well [51], [28], [52]. The full derivation of the general equation can be found in Appendix D of this thesis:

$$\ln\left(\frac{C_e}{C_i}\right) = -k \cdot t$$

Equation 12: General first order equation for batch reactors.

Where; C_e is the concentration of COD in the effluent (mg/L), C_i is the influent concentration of COD (mg/L), k is the reaction rate constant (day⁻¹) and t is the reaction time (days).

To utilize the expression above, the reaction rate constant (k) needs to be determined. This can be done either by plotting the concentration of COD (C) versus time as a function of (C vs Time), ($\ln(C)$ vs Time) or ($1/C$ vs Time). The slope of the plot which yields a straight line is the reaction rate constant. Alternatively, the rate constant can be determined mathematically by substituting all known values into Equation 12. The concentration plots determined to reaction rate constant experimentally have been attached in Appendix D of this report as Figure 42.

Theoretical Rate Constant Determination:

By rearranging Equation 12 and substituting the known values for C_i , C_e and t (from the experiments conducted), we get;

$$\left(\frac{\ln \left(\frac{\frac{320mg}{L}}{\frac{1473.46mg}{L}} \right)}{18days} \right) = k = -0.085day^{-1} \text{ at } 30^{\circ}C$$

(The rate constant in this experiment is negative as it is expressing the consumption of a substance (COD)). The rate constant at 30°C and 16°C was -0.085day⁻¹ and -0.055day⁻¹ respectively. The rate constants determined is comparable to other COD removal rate constants for anaerobic digestion found in literature [11], [52]. The derived reaction coefficient can be substituted into Equation 12 (rearranged) to form the first order kinetic model for COD utilization, illustrated as Equation 13:

$$C_i = C_e * e^{-0.085*t}$$

Equation 13: First order kinetics model for COD utilization in batch reactors.

TSS Removal Model

As mentioned earlier, experimental constraints prevent TSS from being modelled in the batch system.

5.3.2 Biogas Production Model – Batch Configuration

Cumulative biogas production was modelled using first order kinetics (FOK) (similar to the substrate utilization model) and the modified Gompertz (MG) equation - Equation 8.

First Order Kinetics Model

A study by Yusuf and Debora (2011) derived a biogas production equation form first order kinetics. The same model has been considered here to model biogas production from anaerobic digestion of brewery wastewater. This is presented below;

$$B_t = B (1 - e^{-k.t})$$

Equation 14: First order kinetic equation to express biogas generation [53].

Where;

B_t is the volume of biogas generated at any time (ml/g COD)

B is the average biogas production potential of the waste stream (ml/g COD) = 186ml/gCOD at 30°C

k is the reaction rate constant (day^{-1}) = 0.085 day^{-1} at 30°C

t is the time (days)

Substituting all known values:

$$B_t = \frac{186\text{ml}}{\text{gCOD}} * (1 - e^{-0.085.t})$$

Equation 15: First order kinetic model of biogas generation in anaerobic batch reactors.

The second method of modelling biogas production was through the use of the modified Gompertz Equation - Equation 8. Substituting all known experimentally derived variables, $B = 186\text{ml/g COD}$, $R_b = 35\text{ml/day}$, $e = 2.718$, $\lambda = 2$ days, we get;

$$B_t = \frac{186\text{ml}}{\text{gCOD}} * \exp \left\{ -\exp \left[-\frac{35\text{ml/day} \times e}{\frac{186\text{ml}}{\text{gCOD}}} (2 - t) + 1 \right] \right\}$$

The accuracy of these two models are compared below at temperatures of 30°C and 16°C.

It is important to establish that the rational for using first order kinetics to represent the biogas generation instead of zero order kinetics or second order kinetics arises from the data generated during the experiments conducted in this study (*Section 5.3.1*). Comparisons between the rate of biogas generation and substrate utilization was compared to the trends generated by various kinetic models. From this comparison, it was identified that a first order system provided the best fit, followed by a zeroth order reaction and lastly a second order reaction.

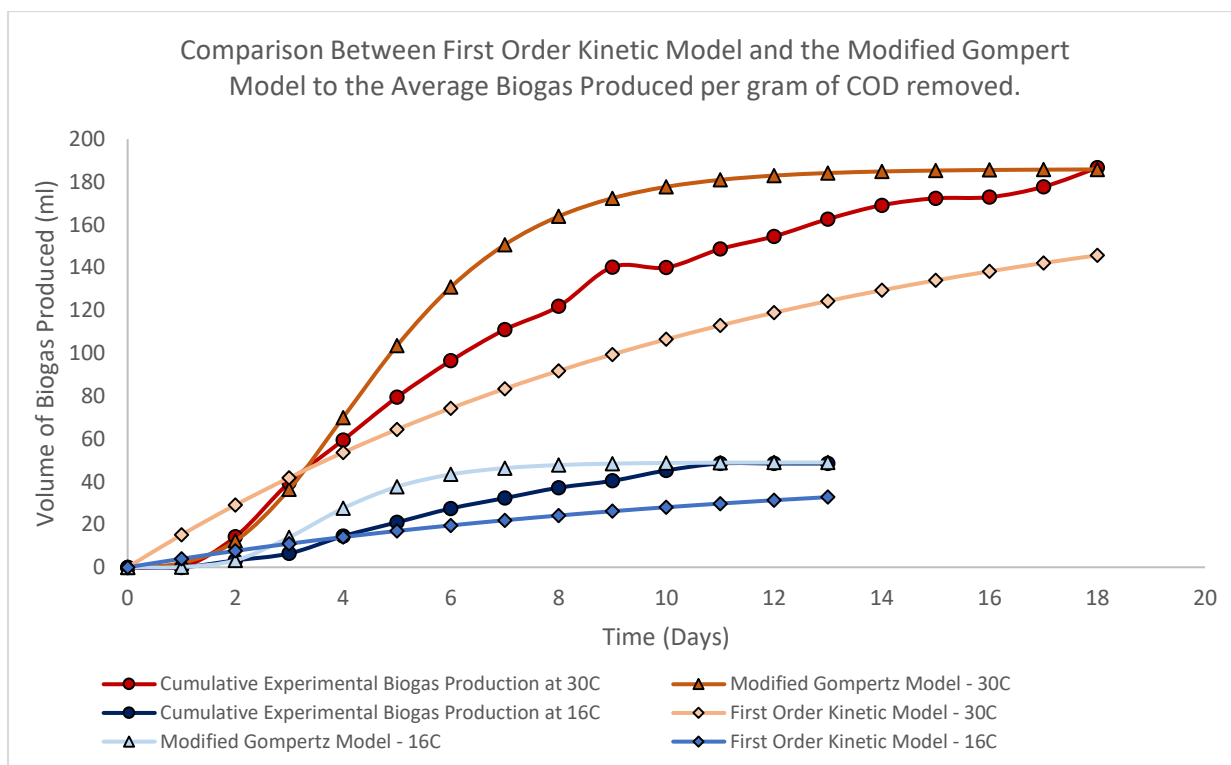


Figure 32: Comparison between the FOK model and the MG model against experimentally produced data at 16°C and 30°C.

Comparing the trends produced in Figure 32 at different temperatures, the modified Gompertz model produced a more accurate estimation of cumulative biogas production at both temperatures. However, regression values between the FOK model and MG indicated that the FOK model produced a more precise regression, 0.979 and 0.945 for the MG model at 16°C and 30°C and 0.993 and 0.985 for the MG model at 16°C and 30°C.

When comparing the results obtained during the batch study with the predicted volume of biogas which should have been generated (from stoichiometric digestion of ethanol and the complete removed of COD from the system to biogas, with minimal assimilation), it's seen that only 20% of the expected volume of biogas was produced.

Some of the differences in biogas production volumes can be attributed to leaks in the equipment used or the effect of pressure inside the eudiometer. In addition, another contributing factor to the lower volume of biogas recorded is the increased solubility of carbon dioxide and

methane at lower temperatures [54], [55]. However, factoring in these variabilities, a large component of the unaccounted biogas is still unknown. This area requires further investigation.

5.3.3 Activation Energy (E_a) and Arrhenius constant (θ) – Batch Configuration.

In addition to describing the utilization of substrate during the anaerobic digestion of brewery wastewater, the rate constant (k) also allows the determination of the reaction activation energy (E_a) through the Arrhenius equation - Equation 4. The activation energy can be described as the energy required to “kick-start” the anaerobic digestion process.

$$k = C e^{-\frac{E_a}{RT}}$$

From the rate constant determined earlier, the activation energy can be determined for this wastewater by rearranging Equation 4.

$$E_a = -\left(\ln\left(\frac{k}{C}\right) \times RT\right) = -\left(\ln\left(\frac{0.085}{\frac{1473.4mg}{L}}\right) \times \frac{8.314J}{mol.K} \times (273 + 30^\circ C)\right) = \frac{24588J}{mol}$$

$$**E_a = 24.59kJ/mol**$$

Therefore, the activation energy (E_a) for Brewery wastewater in a batch reactor at 30°C and 16°C is 24.59kJ/mol and 24.67 kJ/mol respectively. Which places the activation energy needed to anaerobically digest brewery wastewater much lower than the activation energy required for other feed sources such as cow manure, poultry manure and domestic waste which range between 26.60kJ/mol to 37.8kJ/mol - Table 6.

The reason for the lower activation energy of the system can be attributed to the state the usable substrate is presented in. Unlike cow manure and the other wastes listed, brewery wastewater exists in an already hydrolysed state where the COD present has been solubilised. As such, the anaerobic organisms utilize less energy to hydrolyse the waste stream into a soluble, usable, state.

The lower activation energy needed for this process can be associated with the negative Gibbs free energy (ΔG) of the reaction. A negative ΔG favours the spontaneous conversion of reactants into products without the need for any external energy input. The lower E_a is also likely attributed to the waste source already being in a liquid, highly soluble form.

Using the rate constants determined earlier, the Arrhenius constant (θ) for the anaerobic digestion of brewery wastewater as a batch process operating between 16°C and 30°C can also be calculated, from Equation 5.

$$\frac{0.055}{0.085} = \theta^{(291K-303K)}$$

Rearranging the equation above, we get a Arrhenius constant of:

$$\theta = \left(\frac{0.055 \text{ day}^{-1}}{0.085 \text{ day}^{-1}} \right)^{\frac{1}{303K-290.9K}} = 1.031$$

The Arrhenius constant (θ) which can be applied for anaerobic digestion of brewery wastewater in a batch reaction between 16°C and 30°C is 1.031 (≈ 1.03). Generally, the Arrhenius constant (θ) for other wastewater treatment process ranges between 1.020 and 1.10 [11].

5.4 Anaerobic Digestion as a Continuous Process.

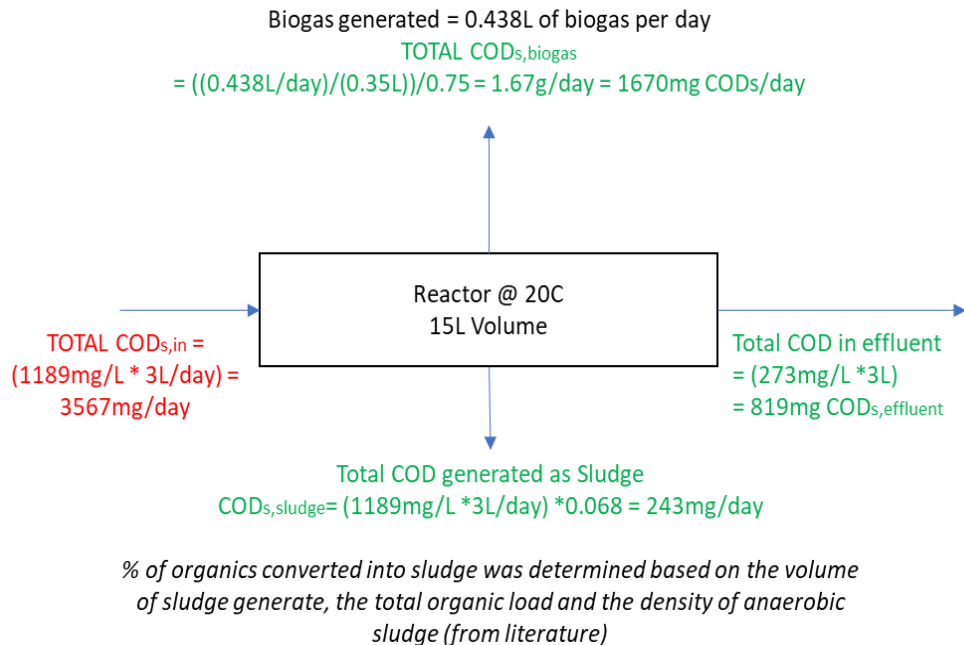
5.4.1 COD Utilization Model – UPFR Configuration

Predicting the effluent concentration of COD at various temperatures and HRTs will provide key information regarding the performance of the AD system and allow an accurate prediction of the downstream effects of an AD+MBBR WWTP configuration.

The mass balance below operates under the same assumptions as those used to model COD movement in the batch reactors.

COD Mass Balance:

Daily continuous mass balance at 5 days HRT



Continuous Reactor Mass Balance:

$\text{COD}_{\text{in}} = \text{COD}_{\text{out}}$

$= (3567\text{mg/day}) - ((1670\text{mg/day}) + (243\text{mg/day}) + (819\text{mg/day})) = 813\text{mg/day unaccounted}$

COD unaccounted for = 23.4%

Figure 33:UPFR mass balance

A mass balance of the UPFR system operating at a HRT of 5 days, indicates that on average 23.4% of CODs being fed into the system was unaccounted for. Unlike the batch system where some COD could have precipitated, the unaccounted CODs likely exists as biogas. Some of the biogas generated would occupy the space between the supernatant surface and the top of the reactor along with the spaces in the biogas lines. However, the most probable explanation for the unaccounted CODs is likely due to biogas being lost via small leaks, which is a common occurrence even in large industrial digestors [56], [57].

Due to the design of the UPFR, the availability of anaerobic biomass differs along the height of the reactor. This is illustrated in Figure 24. This indicates that most of the CODs removal

occurs in the first half of the reactor system. Not only does this indicate that the reactor could possibly be made smaller, but it implies that standard kinetic modelling of the reactor system would not be appropriate, as the removal of CODs is a function of the reactor height and time. In addition to this, axial dispersions and influent and effluent speed variations can cause deviation in a standard kinetic model [11].

To account for these variations, Wehner and Wilhelm (1958) proposed an adaptation of the first order kinetic model [11]. Presented below;

$$\frac{C_e}{C_o} = \frac{4a * \exp(\frac{1}{2d})}{(1 + a)^2 \exp(\frac{a}{2d}) - (1 - a)^2 \exp(-\frac{a}{2d})}$$

Equation 16: Plug flow model developed by Wehner and Wilhelm (1998) [11].

Where:

α is the $\sqrt{1 + 4k\tau d}$

τ is the HRT (days)

d is the dispersion factor = D/vL

v is the fluid velocity (m^2/s)

L is the reactor length (height) = hydraulic radius ($r_{hydraulic}$)= 0.85m

The dispersion coefficient (D) can be calculated using the formula below [11], where Re is the Reynolds number and ν is the kinematic viscosity at the digester's operating temperature.

$$D = 1.01\mu Re^{0.875}$$

$$Re = \frac{4vr_{hydraulic}}{\nu}$$

Table 12 represents the inputs used to model CODs utilization in the UPFR, predicted effluent CODs concentrations and experimental effluent concentrations.

Table 12: Inputs and outputs used to model effluent CODs concentrations versus experimental CODs concentrations.

S.No	Average Influent CODs Conc. (C_i) (mg/L)	HRT (τ) (days)	Temp. ($^{\circ}\text{C}$)	Reaction Rate Constant (k) (day^{-1})	Dispersion Coefficient (D) (m^2/s)	Reynolds Number (Re)	Average Experimental Effluent CODs Conc. ($C_{e,\text{exp}}$) (mg/L)	Predicted Effluent CODs Conc. ($C_{e,\text{pred}}$)
1	1255.0	5	20	0.0119	0.0158	2.14	301.0	323.2
2	1482.8	3	22	0.0158	0.0158	23.14	475.7	397.9
3	1054.8	1	24	0.0176	0.0155	26.65	691.5	322.7
4	1255.0	5	18	0.0079	0.0158	23.15	486.5	346.6
5	1482.8	3	18	0.0122	0.0158	23.14	616.0	413.9
6	1054.8	1	18	0.0157	0.0156	23.14	724.0	325.4

From the model above, the predicted effluent concentration is varied from the experimental results obtained. Variance between the predicted effluent concentration and the experimental concentration varied between 7% and 28% at a HRT of 5 days, 16% to 33% at a HRT of 3 days and 53% and 55% at a HRT of 1 day for the insulated reactor and uninsulated reactor respectively. From these results, it is likely that the variance is likely the effect of several factors, some of which include; 1. Loss of biomass (washout) at lower retention times, 2. Short circuiting due to Brownian motion in the reactor due to the heated feed and the cold reactor, 3. Axial dispersion, 4. Varying concentration of biomass at different heights in the reactor [11]. These results indicate that the model above would be suitable to model the predicted effluent concentration at high HRTs or when there is minimal biomass loss.

Reactor Washout & Failure.

During the period when the AD was operating at a HRT of 1-day, significant volumes of sludge was noticed in the effluent. Analysis of the SRT of the biomass using Equation 9 indicates that;

$$SRT = \frac{VX}{(Q - Q_w)X_e + Q_wX_R}$$

$$\therefore SRT_{@5day\ HRT} = \frac{(15L) \left(\frac{3482mgCOD/L}{1.42mgVSS/mgCOD} \right)}{(3L - 0L) \left(\frac{124mgCOD/L}{1.42mgVSS/mgCOD} \right) + 0} = 122days$$

At a HRT of 5 days, 3 days and 1 day, the SRT varied between was = 122-115 days, 29-26 days and 0.87-0.95 days respectively. As the SRT of the biomass at day 1 was less than the HRT of the wastewater, washout would occur, as observed in this study.

Washout of methanogenic bacteria would have reduced the conversion of VFAs into methane, causing VFA accumulation [11]. This is supported by the reduced pH values observed in both reactors at a HRT of 1 day. The accumulation of VFA would result in souring of the AD and ultimately failure. As such, operating the AD system built at a HRT of 1 day, without a second biomass retention system would lead to digester failure.

5.4.2 Biogas Production Model – UPFR Configuration

Biogas generated from the AD of brewery wastewater at the client's facility is intended for use either as; a cooking gas in the kitchens located on premise, a source of energy to heat the AD unit or as an energy source to power biogas pre-treatment process such as condensers or drip traps for moisture removal [11].

Using raw biogas without any pre-treatment is generally not recommended due to the lower energy density and presence of undesirable substances in the gas [11], such as water vapour, carbon dioxide, hydrogen sulfide, siloxanes etc. [18], [43]. The lower heating value (LHV) of untreated biogas is largely dependent on the concentration of methane in the biogas, however is approximately 22,400kJ/m³ [11], [18]. Methane on the other hand has a higher, LHV of 35,800 kJ/m³ [11].

Results from the experiments conducted indicate that biogas production continuously increases with an increased OLR. While this may be true in some cases (within a narrow operating

window), it is important to note, that an increased OLR can upset the AD and result in hydraulic or substrate overloading [58]. This would ultimately result in biomass washout and the inhibition and death of the methanogenic bacteria [11].

Utilization of the biogas generated is expected to improve the financial viability of this project. To evaluate the potential ad by value of the biogas, the daily volume of biogas needs to be predicted under standard operating conditions. The table below summarises the total volume of biogas generated daily based on the amount of COD removed, the HRT of the reactor and the operating temperature. By scaling this result up to the proposed system size, the volume of biogas generated per-day can be crudely estimated.

Table 13: Summary of daily biogas generation quantities at various HRTs and temperatures for a 15L UPFR AD.

S.No	HRT (Days)	Temperature (C)	Volume of biogas produced per gram of COD removed per day. (L.Biogas/gCODremoved.day)
1.	5	20	0.153
2.	3	22	0.129
3.	1	24	0.299
4.	5	18	0.126
5.	3	18	0.068
6.	1	18	0.152

By assuming that the AD unit operates at 24°C during the summer periods of the year (November to April) and at 18°C during the winter months (May to October), we can predict the volume of biogas produced per year, with a known organic load.

For a full-scale AD operating at a HRT of 5 days, with an average influent feed concentration of 1654.7mg/L and a daily operational volume of (15m³) it is expected that a total volume of 884.66KL/year of biogas will be produced. Assuming that all the methane can be removed from the biogas stream that yields a gross volume of 663.5KL of biomethane per year. This translates to 1658.7 hours of cooking time on a medium flamed gas burner per year, (assuming

that 100L of biogas equates to 15mins of cooking time on a medium flame gas burner) [59]. In addition to this, the yearly savings associated with supplementing the natural gas used for cooking on site can be calculated by assuming that the biogas generated contains 75% methane and 1kWh of energy = \$0.1364 [60]. From this;

$$1 \text{ m}^3 \text{ of Natural Gas} = 8,8 \text{ kwh [61]} = \$1.200/\text{m}^3$$

$$1\text{m}^3 \text{ of CH}_4 = 11.12\text{kwh [62]} = \$1.517/\text{m}^3$$

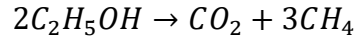
$$1\text{m}^3 \text{ of biogas (75\% methane composition)} = 8.34 = \$1.138/\text{m}^3$$

$$\text{Total \$ savings from using the biogas generated as a cooking gas fuel source is } (884.66\text{m}^3/\text{yr} * \$1.138/\text{m}^3) = \$1006.4 \text{ per annum}$$

Comparing the theoretical volume of biogas which should be produced (if the feed wastewater was only ethanol) and the volume of biogas which was actually produced, less than 33% of the predicted biogas was generated from both the AD units. As anaerobic systems only assimilate a small portion of the organic load, the remaining CODs removed must be converted into methane and carbon dioxide if the digestion process goes to completion [11], [12]. The reduced volume of biogas captured likely indicates that the biogas generated was lost due to entrapment or leaks in the AD unit.

As the methane is a highly flammable gas [11], [63] and has approximately 30 times the greenhouse effect of carbon dioxide, it is imperative that the biogas generated is collected efficiently and safely to prevent severe negative environmental consequences [11], [39]. Preventing leakages and losses of biogas will also increase the volume of biogas which can be used for cooking.

Gas chromatography analysis of the biogas generated from the UPFR suggested that 76.2% of the gas fraction was methane and 7.6% was carbon dioxide. Assuming the wastewater feed was only composed from ethanol, AD of the ethanol would yield a biogas which was composed of 75% methane and 25% carbon dioxide, via stoichiometry.



Equation 17: Anaerobic digestion of ethanol.

An evaluation of the elevated methane composition and reduced carbon dioxide composition likely indicates that most of the carbon dioxide generated was dissolved into the supernatant of the anaerobic digestion. This would causally reduce the carbon dioxide fraction and increase the methane fraction.

5.4.3 TSS Reduction Model – UPFR Configuration

TSS reduction in the UPFR was modelled using the same process used to model TSS concentrations in the MBBR unit. It is important to note that this model is only applicable to the UPFR systems used in this study and that is operating at a HRT of either 3 days or 5 days.

Table 14: TSS reduction coefficients at different temperatures and HRT.

HRT (Days)	Temperature (°C)	TSS Reduction Coefficient (r_{TSS})
5	20	0.896
5	18	0.783
3	22	0.660
3	18	0.553

TSS Reduction Model for UPFR:

$$TSS_{out} = (COD_{in} * f_{cv,COD:TSS}) * (1 - (r_{TSS}))$$

Equation 18: TSS reduction model for AD

5.4.4 Sludge Generation Model – UPFR Configuration

Sludge generation is a key consideration which needs to be accounted for in all practical systems [11], [64]. Improper management of sludge can result in operational complications. Sludge generation results determined from experimental testing indicated that approximately 4.6% of the organic load is converted into sludge. However as mentioned earlier, this does not account for any biomass lost via washout at a HRT of 1 day. Thus, it would be prudent to use

a “safety factor” (SF) and increase the conversion percentage of organic load to sludge to maintain the precautionary principles. However, this is subjective to the application of the AD system. As such, for the purposes of this thesis, the safety factor has been omitted.

The model to predict sludge generation, is presented below:

$$\text{Mass of sludge generated} = \text{organic load} * 4.6\%$$

Equation 19: Sludge generation model.

5.5 Activation Energy (E_a) and Arrhenius constant (θ) – UPFR Configuration

Using the same process of determining E_a and θ , as that used in the batch study, the resultant values at different HRTs and temperatures are;

Table 15: Activation energy and Arrhenius constant of AD of brewery wastewater.

Description	Operating Parameters	Insulated Reactor	Un-Insulated reactor
Activation Energy (kJ/mol)	5 Day HRT	21.09	20.44
	3 Day HRT	20.62	20.21
	1 Day HRT	19.61	19.32
Arrhenius constant (θ)	5 Day HRT Between 15.4C and 20.1C		1.09
	3 Day HRT Between 17.7C and 20.9C		1.09
	1 Day HRT Between 24.2C and 23.2C		0.50

The results indicated in Table 15 indicates that the activation energy reduces as HRT and temperature increases. The difference in E_a is most likely due to the quiescence of anaerobic bacteria and lag time.

A study conducted by Roslev and King in 1995 established that methanophiles were able to enter a state of dormancy where there was no metabolic activity when they were starved aerobically and anaerobically [65]. In fact, up to 80% of bacteria in the wild can appear to be metabolically inactive [66]. The study by Rosley and King indicates that these types of bacteria were able to enter a period of dormancy when substrate concentrations were low, without

dying. To revive these bacterial cells, energy is needed. This extra energy required to ‘activate’ the dormant methanogens may contribute to the higher activation energy determined between the batch studies and the UPFR. In addition to this, as the lag duration reduces due to the increased organic loading rate (from more frequent feeding in the UPFR), the period of dormancy of these methanogens may also reduce, requiring less energy to activate them. This may be an indication of why the activation energy needed at different HRTs reduces as the detention times also reduce. This also would possibly explain the difference in the E_a observed between the batch and UPFR study.

The largest point of interest is the Arrhenius constant at a HRT of 1 day. As the Arrhenius constant is a function of the rate constants, determined by the average influent and effluent COD concentrations determined during testing, it is likely that biomass lost as washout affected the rate constant, resulting in a Arrhenius constant which is nearly half of the values at a 5- and 3-day HRT.

5.6 Comparison Between the Current WWTP and the Proposed System.

By substituting a range of arbitrary COD concentrations to simulate the brewery wastewater characteristics into the proposed AD+MBBR system, and the MBBR system, we can predict the downstream effects onto the UF membranes. This has been represented below:

Table 16: Comparison between the current MBBR system versus the proposed AD+MBBR system at different HRT.

Influent Conc. (mg/L)	WWTP Configuration	Temperature (C)	Predicted COD Conc. (mg/L)	Predicted TSS Conc. (mg/L)	COD Comparative Reduction (%)	TSS Comparative Reduction (%)
1200	MBBR	17	22.7	63.5	-	-
	AD+MBBR - 5 Day HRT	20	5.9	16.4	74.0	74.2
	AD+MBBR - 3 Day HRT	22	6.3	17.6	72.2	72.3
1500	MBBR	17	28.3	79.3	-	-
	AD+MBBR - 5 Day HRT	20	6.6	17.8	76.6	77.6
	AD+MBBR - 3 Day HRT	22	7.6	21.2	73.3	73.3
1800	MBBR	17	34.0	95.2	-	-
	AD+MBBR - 5 Day HRT	20	8.4	23.4	75.3	75.4
	AD+MBBR - 3 Day HRT	22	8.9	24.9	73.9	73.9

Via the mathematical models developed, a comparison between the current MBBR system versus the proposed AD+MBBR system at similar influent COD concentrations, the proposed system is able to achieve between a 73% to 77% improvement on the quality of the wastewater prior to UF.

In addition, the predicted TSS concentrations at the end of the AD+MBBR process (before UF) suggest that with the proposed system in place, UF may no longer even be required. This is considered as the brewery has a TSS discharge approval of $\leq 30\text{mg/L}$ of TSS [4]. This would reduce the yearly expenditure associated with maintaining the UF system by as much as AUD94,600, as labour costs, chemical costs, aeration costs and electricity costs are reduced significantly.

To validate the models generated, it is strongly recommended that a downstream UF or an MBBR+UF pilot plant study be conducted in the future. Effluent generated from the AD+MBBR unit would ideally be passed through the UF membranes, to assess the effect the generated effluent has on the membranes, as well as the maximum achievable COD removal

which can be achieved by the system. Should the pilot trials prove successful, detailed cost analysis and financial evaluation of the system can be assessed, as possible future work.

5.7 Effect of Proposed System on UF Membranes

While it is difficult to quantify the effect of the effluent generated from the current MBBR unit on the UF membranes. We can estimate the effect the proposed treatment system will have on the UF membranes through several assumptions, listed below;

1. MBBR unit and the proposed system (AD+MBBR) unit are operating at steady state.
I.e. Both systems have identical OLRs, treats the same volume of wastewater with identical characteristics.
2. UF membrane degradation is only a function of the TSS concentration in the effluent stream.

Based on the assumptions above, it can be argued that if the UF membranes have a lifespan of 1 year under current TSS loading conditions, reducing the TSS load by half should in theory double the expected lifespan from 1 year to 2 years. From this relationship, reducing the TSS load by 75% using the proposed AD+MBBR system should increase the lifespan of the UF membranes by 3-4 years. However, until the system is actually trialed and mathematically modelled, it is difficult to provide a definite projected lifespan.

However, improving the lifespan of the UF membranes by one year, will result in a saving of AUD25,000 at a minimum. This translates to a saving of between AUD37,500 and AUD43,750 per year, reducing the membrane operational costs by up to 87.5% (excluding other operational costs).

5.8 Practical Engineering Lessons

Several design considerations can be made based on the outcomes of this project, assuming a similar AD system which was used in this pilot study was applied to the brewery.

1. Firstly, when COD removal is concerned, a 40% smaller reactor can be used provided it is insulated. If the reactor was to be heated, the reactor volume could be made smaller or the HRT could potentially be reduced (subject to hydraulic or organic overloading).
2. For maximum SS removal, a reactor with a longer HRT would be preferred as it would provide the suspended particles a longer settling time.
3. Alkalinity will likely be required to neutralize the acidity of the wastewater stream and the reactor to prevent souring.
4. Biogas generated has the potential of being a high methane source (up to 75% methane), as H_2S was not detected by GC-TCD, a H_2S scrubber may not be required. However, this should be verified using a FTIR instrument.
5. If the HRT is desired to be reduced to a period shorter than 1 day, an external sludge recycle system will be needed. Otherwise there is a high likelihood of reactor washout.
6. The reactor will need to consider the accumulation of sludge (4.6% of the daily organic load).
7. Methane is a highly flammable source, care must be taken to prevent any dangerous situations from possibly arising, such as air mixing with the biogas to form an explosive environment.

Chapter 6: Conclusion

Fouling of UF membranes at a local brewery resulted in significant increase in operational expenditure, in excess of \$94,600 per annum. The frequent fouling of the UF membranes were attributed to the high COD concentration of wastewater and TSS generation in the onsite WWTP. This project was aimed at; evaluating the operational viability of using anaerobic digestors to pre-treat brewery wastewater for COD and TSS removal to prevent fouling of the UF membranes. The downstream effect of the AD was predicted using several mathematical models.

Results from this project indicated that an AD operating at a HRT of 5 days was able to achieve an average COD reduction of 75.9% and 61.2% at 20°C and 18°C respectively. At a HRT of 3 days, the reduction in COD reduced to 67.9% and 58.5% at temperatures of 22°C and 18°C respectively. However the lowest removal of COD was observed at a HRT of 1 day, where both reactors only removed between 31.4% to 34.4% of the pollutant at a temperature of 24°C. The low COD removal at a HRT of 1 day was attributed to washout of anaerobic biomass from the reactor. This was supported by higher TSS concentrations (an increase of 13%-32%) in the effluent compared to the influent. Unlike COD removal, TSS was less affected by temperature, but more so affected by the HRT of the AD, with a reduction of 89.6% and 66% at a HRT of 5 days and 3 days respectively.

Mathematical modelling of the downstream effects of the proposed AD+MBBR system, indicates that the proposed system will be able to remove between 73% - 75% more COD and generate 73% to 76% less TSS at the end of the MBBR treatment process prior to UF than the current system. The reduction in TSS concentrations is project to increase the UF membranes current lifespan from 1 year to 3-4 years. In addition to this, the predicted TSS concentrations post AD and MBBR treatment strongly suggest that the UF process can be decommissioned as

any residual TSS is lower than the brewery's allowed dischargeable limit. Pending local and state approvals, this has the potential of saving the brewery between AUD37,500 and up to AUD94,000 per year. Biogas generated from the AD process also has the potential of improving the financial viability of the project by subsidizing the use of LNG for cooking, with a 15m³ reactor predicted to be able to provide 1659 hours of continuous cooking time for a single gas burner per year, at minimum. This translates to a savings of AUD1006 per year.

Results from this study also suggest that the activation energy required for AD of brewery wastewater is between 20.41kJ/mol.K and 20.09 kJ/mol.K respectively. The differences between the activation energy determined by the batch study and the UPFR were statistically not significant ($p < 0.05$) and places the activation energy of AD of brewery wastewater lower than other waste streams such as municipal waste, cow dung or poultry waste. AD Arrhenius constants were observed to fluctuate based on the reaction rate constant, ranging between 1.03 and 1.09 at 30°C and 22°C respectively.

In conclusion, considering the unique operational issues faced by the client, results from this study suggest that AD of brewery wastewater is an operationally and economically viable solution in reducing the COD and TSS concentrations of the raw wastewater and of the wastewater being treated in the current MBBR unit. This is the case with significant operational and expenditure benefits predicted.

Chapter 7: References

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Chapter 8: Appendix

Appendix A – MBBR Schematics

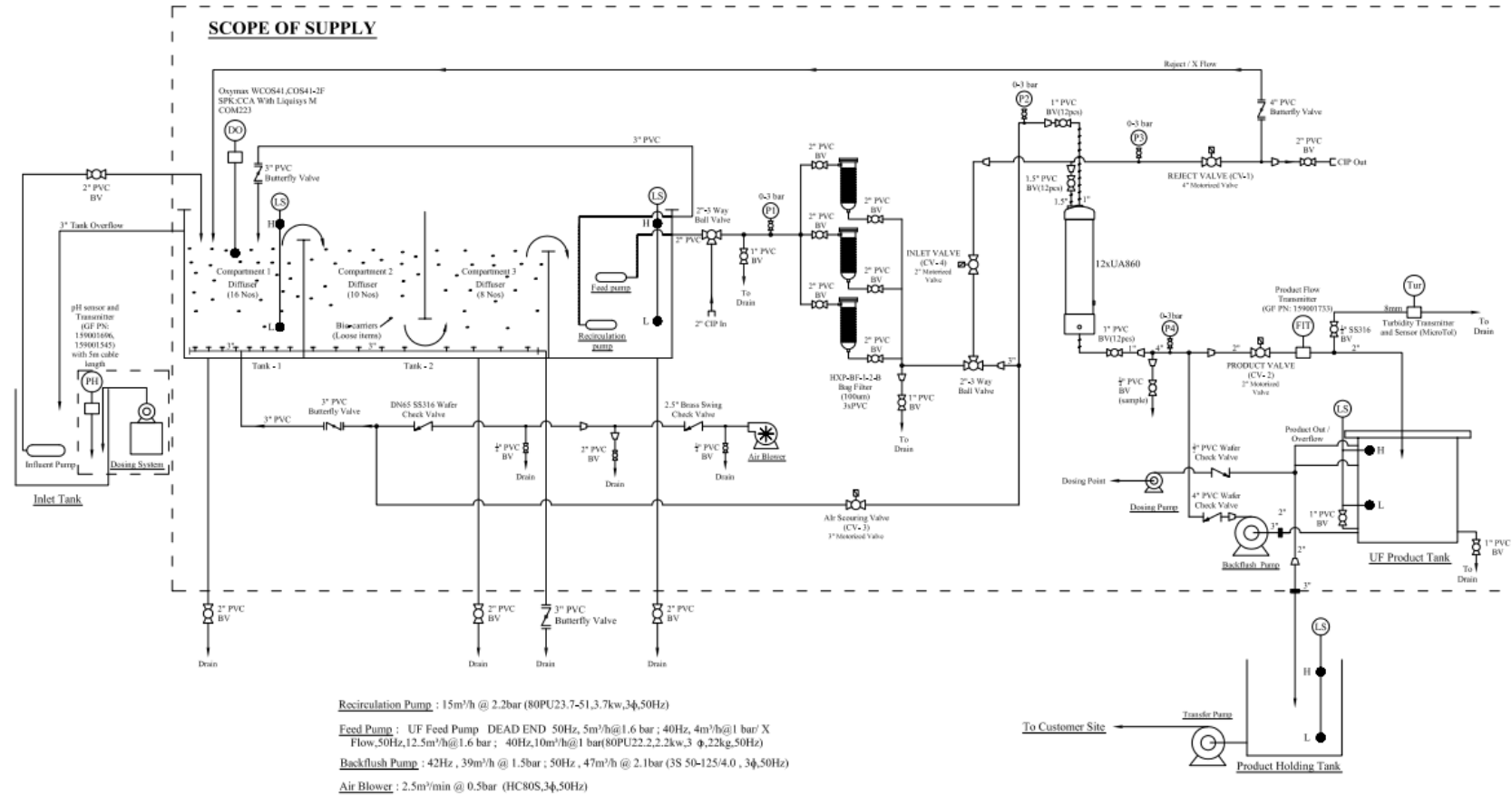


Figure 34: Process flow diagram of the Klar Bio 40 MBBR used at the brewery [67], [68].

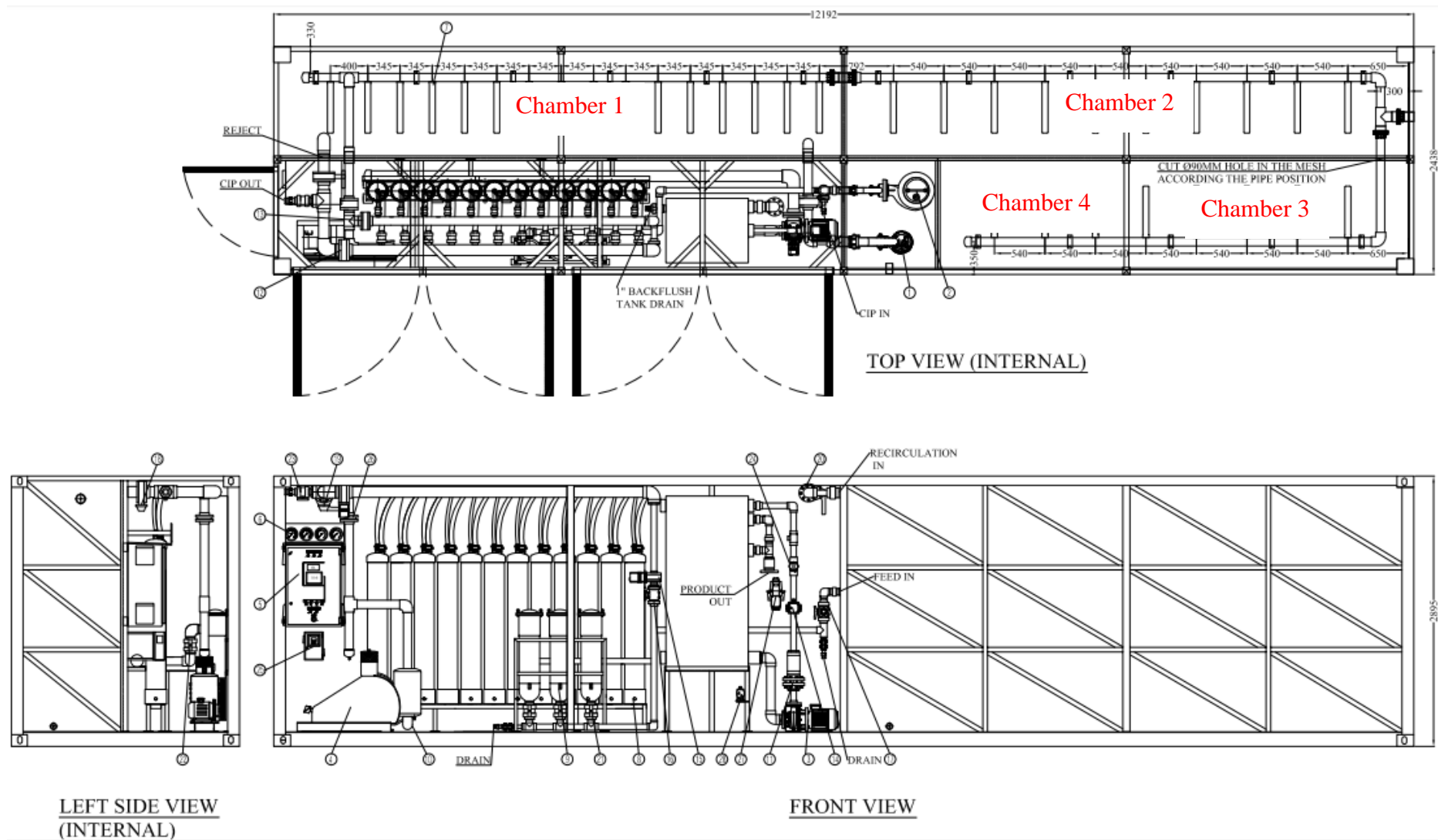


Figure 35: Klar Bio MBBR schematics [67], [68].

Appendix B – Wastewater Testing Methods

Table 17: Methods used to test wastewater characteristics.

S.No	Parameter	Method of Testing	Test Location	Samples Tested
1.	Total Chemical Oxygen Demand (CODt)	<ul style="list-style-type: none"> Tested using HACH COD high range chemical reagents; <ul style="list-style-type: none"> Reagent – 2125825: COD Digestion Vials, Low Range Digestor – DRB200 - LTV082.52.30001 Measurement - HACH handheld spectroscope. Tested using MERCK COD high plus range (25-1500mg/L) chemical reagents. 	Laboratory Testing	<ul style="list-style-type: none"> Raw Wastewater MBBR Reactor
2.	Soluble Chemical Oxygen Demand (CODs)	<ul style="list-style-type: none"> Tested using HACH COD low range chemical reagents; <ul style="list-style-type: none"> Reagent – 2125825: COD Digestion Vials, Low Range Digestor - DRB200 - LTV082.52.30001 Measurement - HACH handheld spectroscope. 	Laboratory Testing	<ul style="list-style-type: none"> Raw Wastewater MBBR Reactor
3.	Total Suspended Solids (TSS)	<ul style="list-style-type: none"> Gravimetric Analysis 	Murdoch University	<ul style="list-style-type: none"> Raw Wastewater MBBR Reactor Anaerobic Digestor
4.	Reactive Phosphorus (orthophosphates) (PO_4^{3-})	<ul style="list-style-type: none"> Tested using HACH PO_4^{3-} high range chemical reagents; <ul style="list-style-type: none"> Reagent – PO_4^{3-} Box 73 (0-100mg/L) Digestor - DRB200 - LTV082.52.30001 Measurement - HACH handheld spectroscope. 	Laboratory Testing	<ul style="list-style-type: none"> Raw Wastewater Anaerobic Digestors MBBR Reactor
5.	Nitrites (NO_2^-)	<ul style="list-style-type: none"> Tested using HACH NO_2^- high range chemical reagents; <ul style="list-style-type: none"> Reagent – NO_2^- Box 83 (I.D: 2608345) Measurement - HACH handheld spectroscope. 	Laboratory Testing	<ul style="list-style-type: none"> Raw Wastewater Anaerobic Digestors MBBR Reactor
6.	Total Nitrogen (TN)	<ul style="list-style-type: none"> Tested using HACH TN⁻ high range chemical reagents; <ul style="list-style-type: none"> Reagent – Total Nitrogen Box 21 & 40 Digestor - DRB200 - LTV082.52.30001 Measurement - HACH handheld spectroscope. 	Laboratory Testing	<ul style="list-style-type: none"> Raw Wastewater Anaerobic Digestors MBBR Reactor

7.	Total Phosphorus (TP)	<ul style="list-style-type: none"> • Tested using HACH TP high range chemical reagents; <ul style="list-style-type: none"> ○ <i>Reagent – Total Phosphorus Box 72</i> ○ <i>Digester - DRB200 - LTV082.52.30001</i> ○ <i>Measurement - HACH handheld spectroscope.</i> 	Laboratory Testing	<ul style="list-style-type: none"> • Raw Wastewater • Anaerobic Digestors • MBBR Reactor
8.	pH	<ul style="list-style-type: none"> • Tested using YSI -Prod DSS sensor – pH / Temperature probe. 	Onsite Field Test	<ul style="list-style-type: none"> • Raw Wastewater • MBBR Reactor • Anaerobic Digestors
9.	Temperature (C)	<ul style="list-style-type: none"> • Tested using YSI -Prod DSS sensor – pH / Temperature probe. • Analogue alcohol filled thermometer 	Onsite Field Test	<ul style="list-style-type: none"> • MBBR Reactor • Anaerobic Digestors
10.	Conductivity (μS/cm)	<ul style="list-style-type: none"> • Tested using YSI -Prod DSS sensor – Conductivity probe. 	Onsite Field Test	<ul style="list-style-type: none"> • MBBR Reactor
11.	Oxidation Reduction Potential (ORP)	<ul style="list-style-type: none"> • Tested using YSI -Prod DSS sensor – ORP probe 	Onsite Field Test	<ul style="list-style-type: none"> • Raw Wastewater • MBBR Reactor
12.	Ammonium (NH ₄ ⁺)	<ul style="list-style-type: none"> • Tested using YSI -Prod DSS sensor – NH₄⁺ probe 	Onsite Field Test	<ul style="list-style-type: none"> • Raw Wastewater • MBBR Reactor
13.	Nitrates (NO ₃ ⁻)	<ul style="list-style-type: none"> • Tested using YSI -Prod DSS sensor – NO₃⁻ probe 	Onsite Field Test	<ul style="list-style-type: none"> • Raw Wastewater • MBBR Reactor
14.	Turbidity (NTU & TSS)	<ul style="list-style-type: none"> • Tested using YSI -Prod DSS sensor – Turbidity probe 	Onsite Field Test	<ul style="list-style-type: none"> • Raw Wastewater • MBBR Reactor
15.	Total Dissolved Solids	<ul style="list-style-type: none"> • Tested using YSI -Prod DSS sensor – Conductivity probe 	Onsite Field Test	<ul style="list-style-type: none"> • Raw Wastewater • MBBR Reactor • Anaerobic Digestors

Appendix C – Additional Experimental Results.

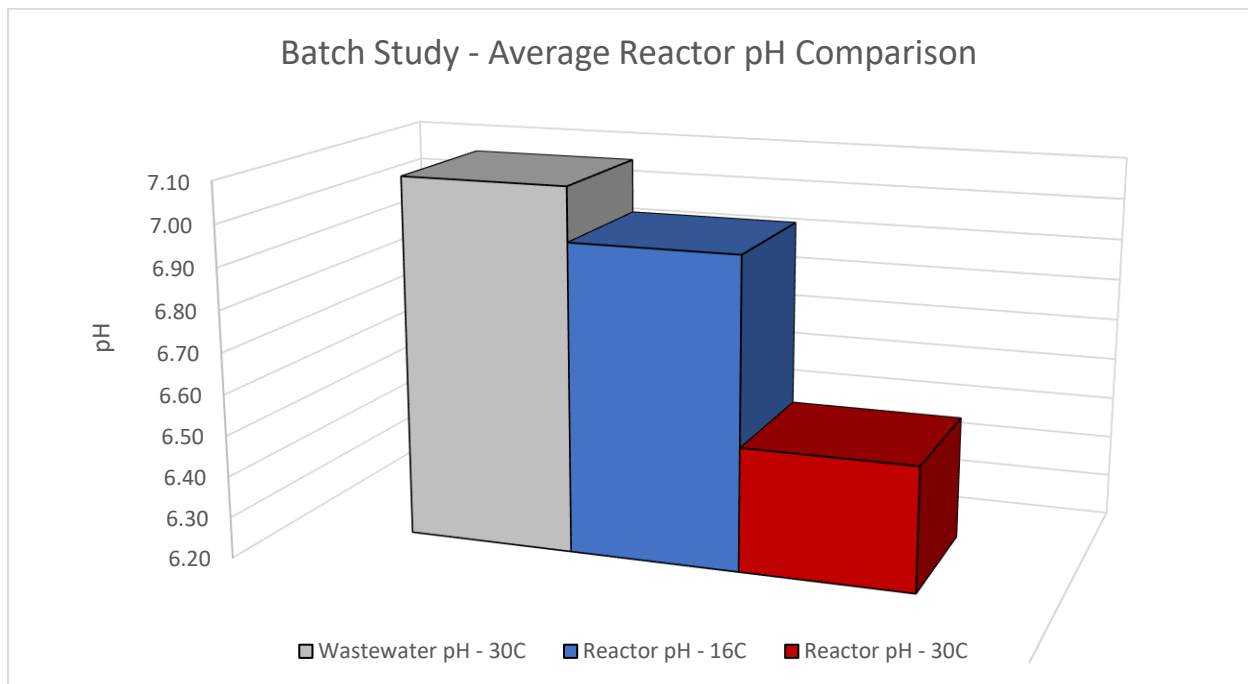


Figure 36: pH of variable temperature AD of brewery wastewater.

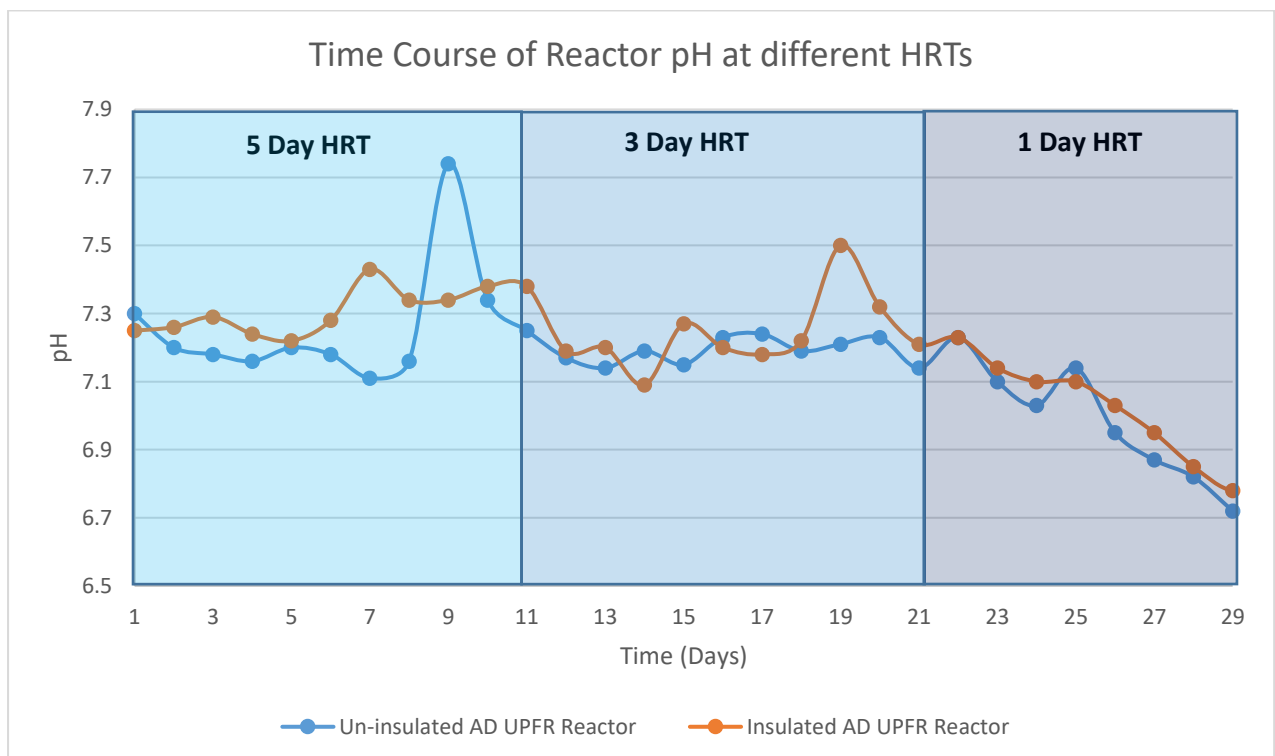


Figure 37: Time course snapshot of reactor pH at different hydraulic residence times.

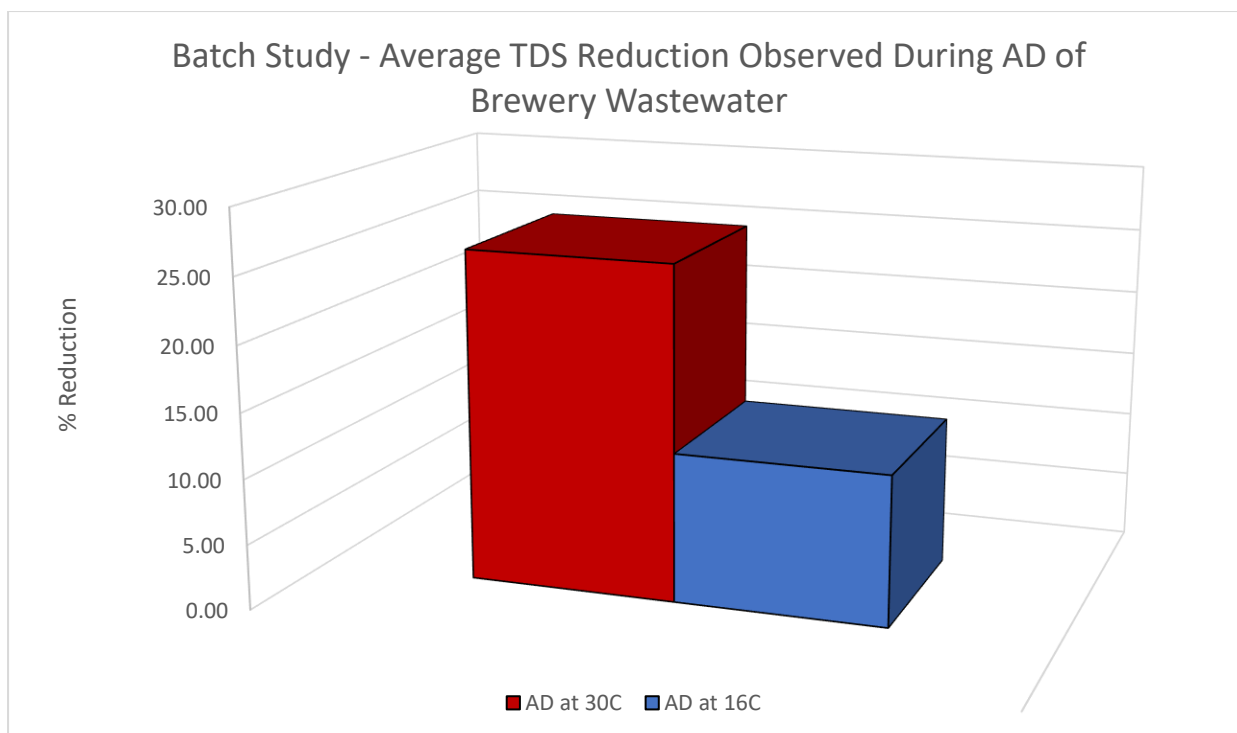


Figure 38: Average TDS reduction observed during AD of brewery wastewater at different temperatures during the batch study.

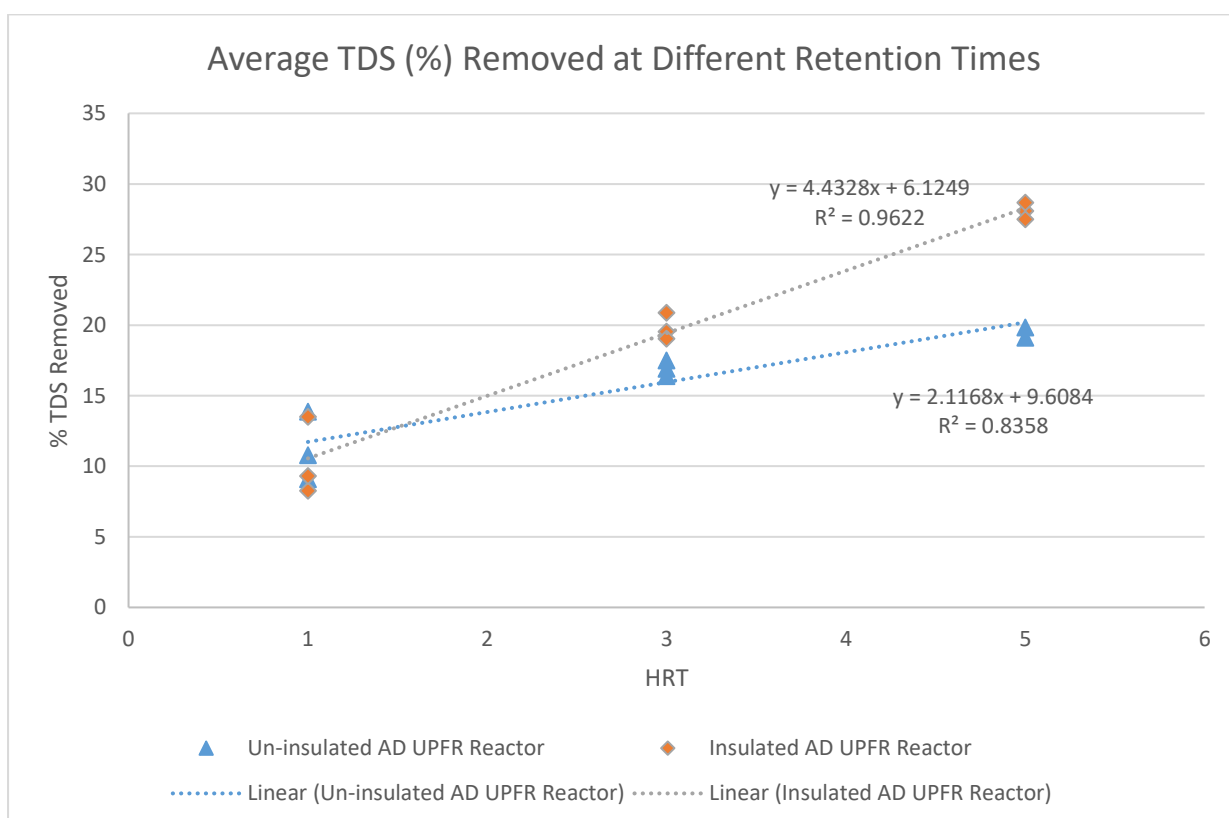


Figure 39: Average TDS reduction observed during AD of brewery wastewater at different temperatures during the UPFR study.

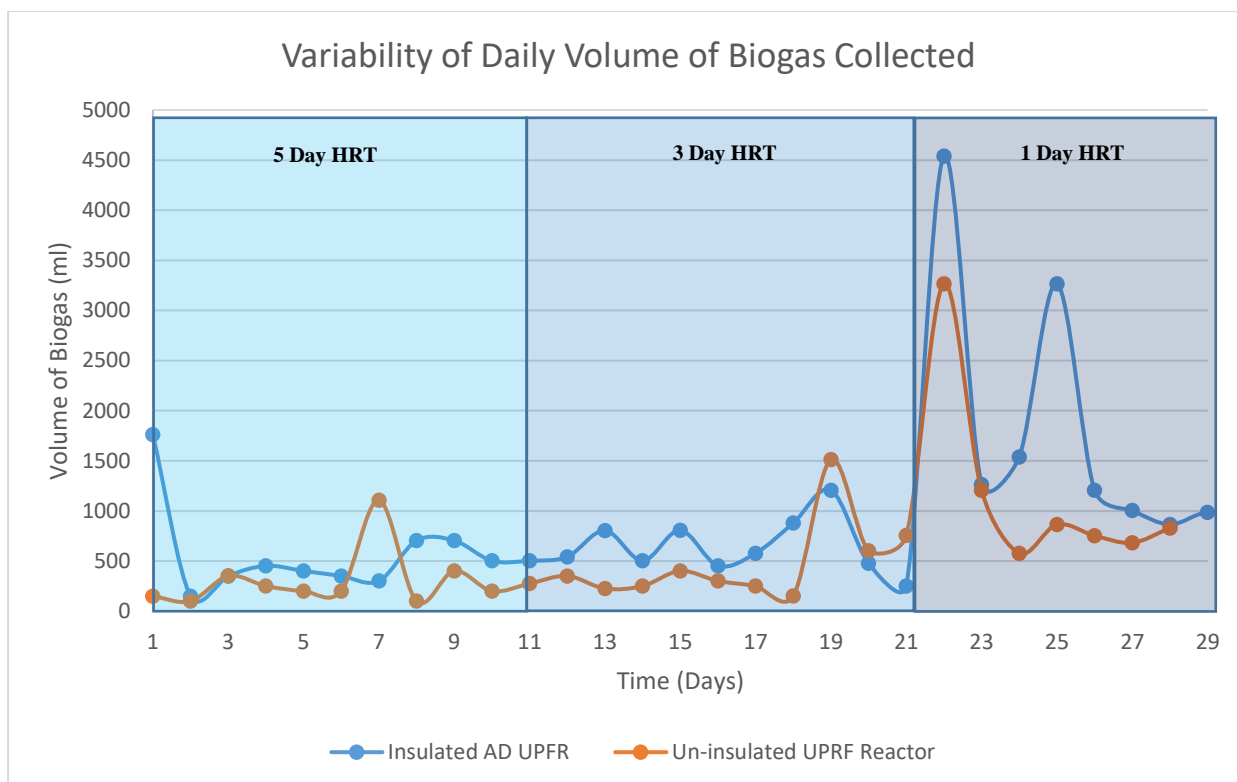


Figure 40: Variability of daily biogas produced at different HRTs.

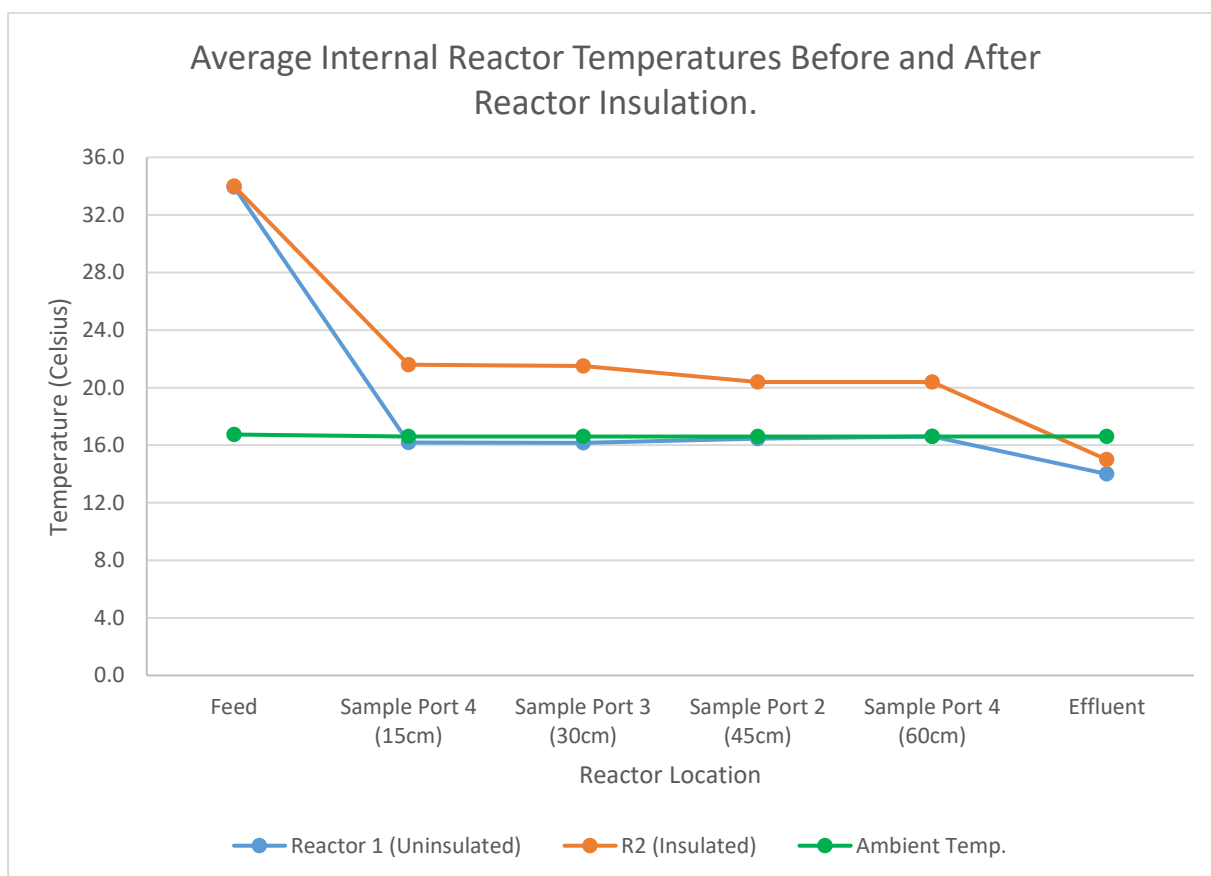


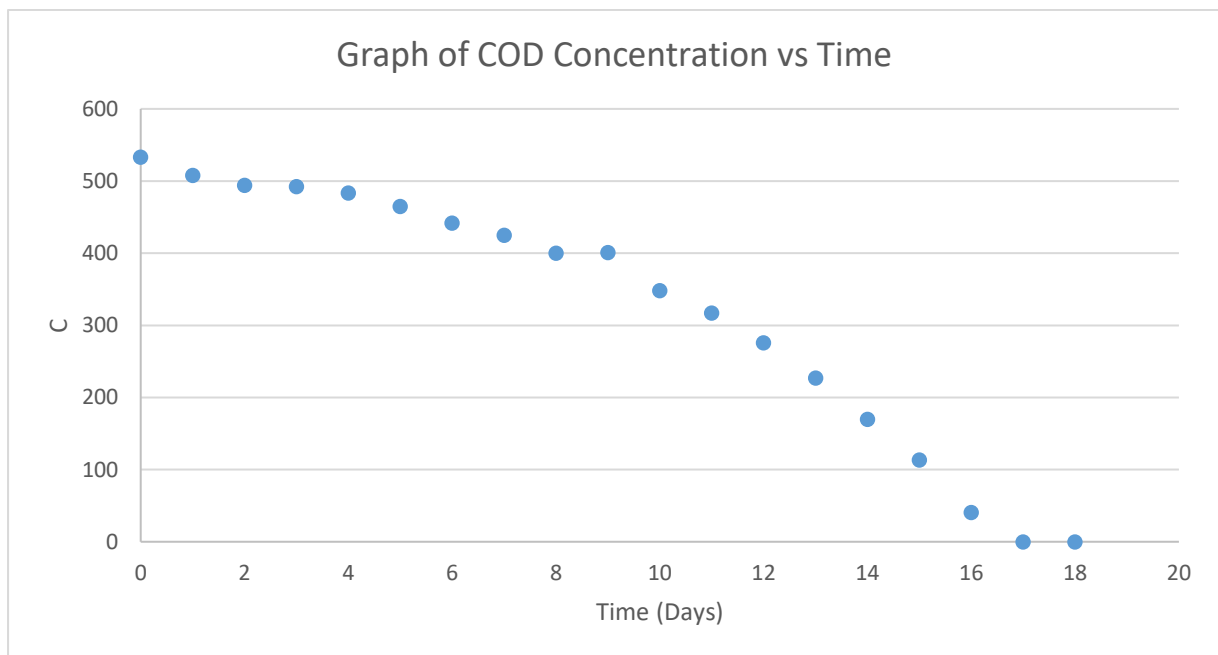
Figure 41: Effect of insulation on reactor temperatures at a HRT of 3 days.

Appendix D – Reaction Kinetics

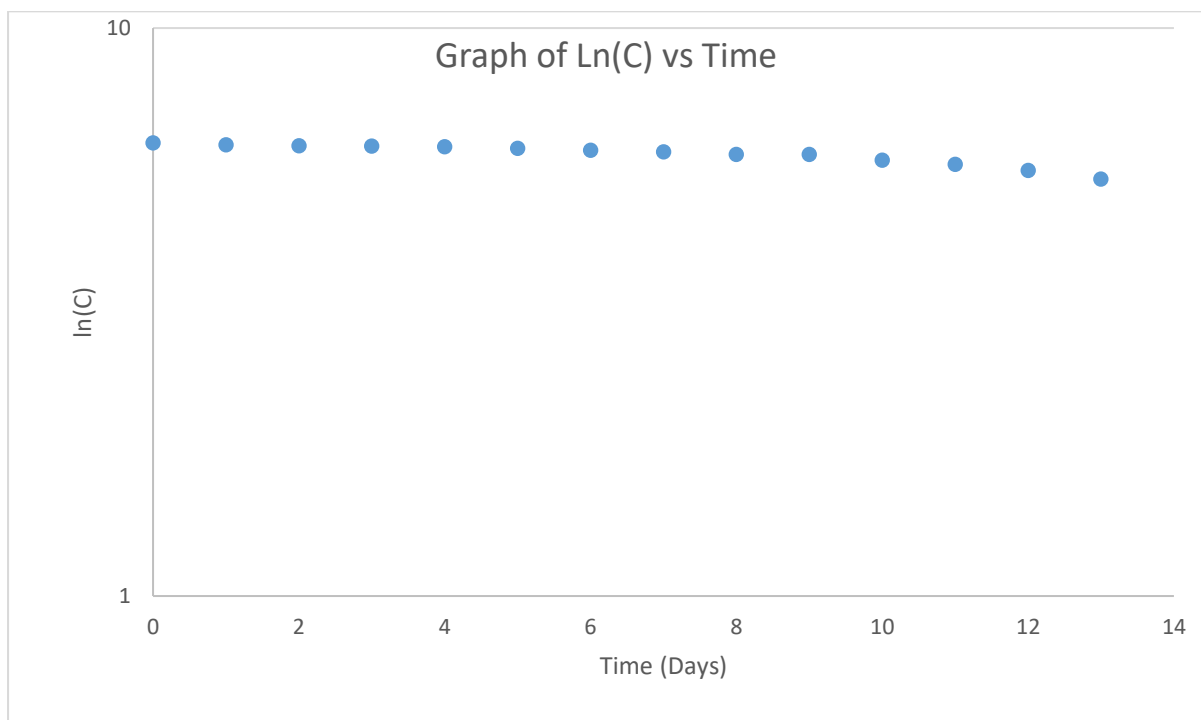
Experimental Derivation of Reaction Kinetics – Batch Study

Figure 42: A,B,C - Kinetic evaluation of experimental data.

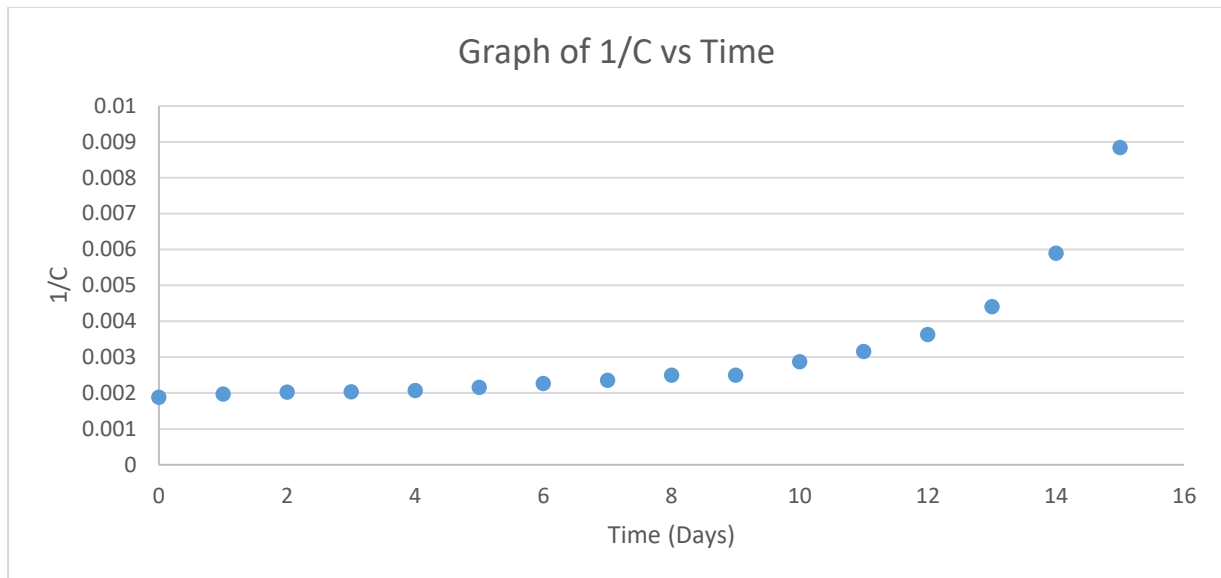
A. Graph of Concentration vs Time.



B. Graph of Natural log of COD Concentration versus Time.



C. Graph of Inverse COD Concentration versus Time.



Derivation of General First Order Kinetics Equation

Mass Balance

Accumulation rate within system boundaries

= flow rate of reactant into the system boundary

– flow rate of reactant out of the system boundary

+ rate of reactant generation.

Representing the reaction mass balance symbolically.

$$\text{Accumulation} = \text{Inflow} - \text{Outflow} + \text{Generation}$$

$$V * \left(\frac{dC}{dt} \right) = Q_i \cdot C_i - Q_e \cdot C_e + r(C) \cdot V$$

Where;

$\left(\frac{dC}{dt} \right)$ - the change in reactor concentration over time (mg/L.s)

Q_i and Q_e - inflow rate and outflow rate (L/s)

C_i and C_e - influent and effluent concentrations respectively (mg/L)

V - reactor volume (L)

$r(C)$ - reaction rate expression. (dependant on the order of reaction)

Making Simplifying Statements:

In the case of batch reactors, some simplifying statements can be made. As they system deals with the reaction process as a batch, there is no inflow or outflow of reactants ($Q = 0$). This simplifies the equation above to;

$$V * \left(\frac{dC}{dt} \right) = 0.C_i - 0.C_e + r(c).V = r(c).V$$

$$\therefore \left(\frac{dC}{dt} \right) = r(c).$$

As the utilization of substrate is not a linear process, and is dependent on the concentration of the reactant available, a pseudo-first order relationship can be established, where;

$$r(c) = -kC$$

Substituting the rate expression above into Equation 5, we get;

$$\begin{aligned} \frac{dC}{dt} &= -kC \\ \int_{C_i}^{C_e} \frac{dC}{C} &= -k * \int_{t_0}^t dt \end{aligned}$$

Where, at $t_0 = 0$ days;

Solving the above we get;

$$\ln(C_e) - \ln(C_i) = -k * (t - 0) = -k.t \quad - (A)$$

Simplifying (A), we get;

$$\frac{C_e}{C_i} = e^{-k.t}$$

$$\ln \left(\frac{C_e}{C_i} \right) = -k.t$$

Appendix E – Additional Information.





Figure 43: Concrete settling tank post phosphorus coagulant and chlorine dosing, MBBR UF system, AD reactors being fabricated, small bag filter used before MBBR treatment [6].

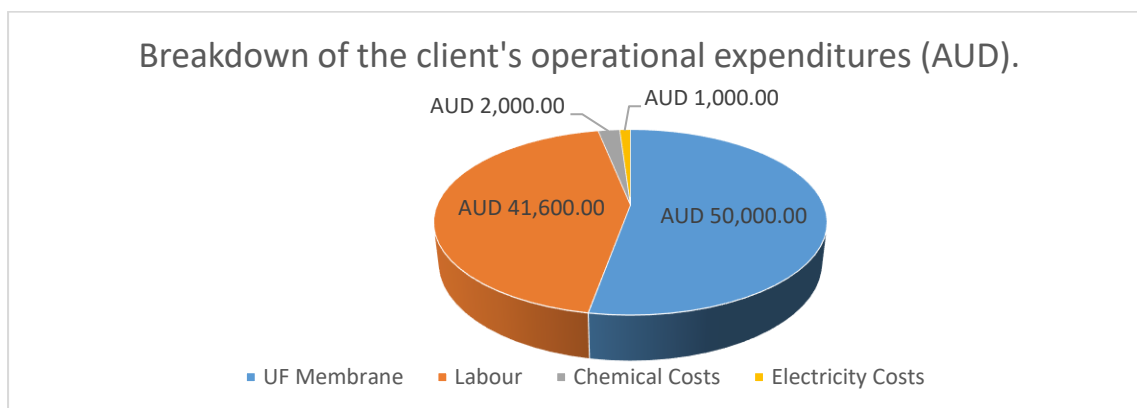


Figure 44: Breakdown of the client's operational expenditure.

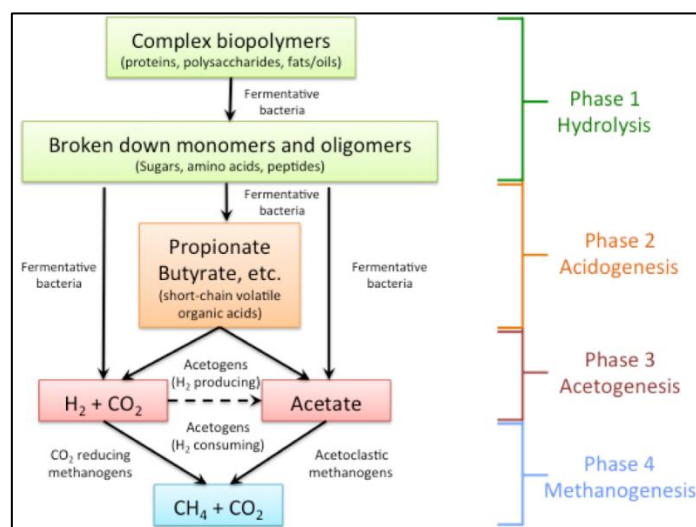


Figure 45: Illustration of the AD process [39].